

This presentation describes the status of spectral line parameters of atmospheric molecules in the near and mid infrared and our ability to measure them in terms of both precision and accuracy. Jean-Marie Flaud presented the status of positions and intensities in the previous talk, so the other parameters will be the center of attention here.

The Lorentz broadening coefficients are very important to most atmospheric experiments. For experiments that measure the integrated absorption over a bandpass much broader than a spectral line, the halfwidth has little importance for weak spectral lines, but is as important as the intensity for strong spectral lines where the Lorentz width is comparable to, or greater than, the Doppler width. For experiments that resolve spectral line shapes, the Lorentz halfwidth is always important except high in the atmosphere where the Doppler width is much greater than the Lorentz width.

Figure 1 is a rather old graph (perhaps 10 or 15 years old) displaying the manner in which halfwidths were measured at the time. The vertical axis is the Lorentz halfwidth and the horizontal axis is the pressure of the gas in the cell. In this particular case the absorbing gas is methane and the broadening gas is air. Three spectral lines are plotted in the three colors. Each line was measured on three different spectra. The width is linearly proportional to pressure, so the width at any pressure can be specified by merely giving the slope of the line in this plot. The line must pass through the origin. Each spectral line has a different slope. The points show some scatter from the line due to the uncertainty of each measurement.

The slopes measured in this manner are defined as the Lorentz halfwidth coefficient of the spectral line. How well known are the halfwidths of the spectral lines of interest to the atmospheric scientist?

One popular source of halfwidths of infrared spectral lines is the HITRAN 2000 database. Since the 1986 edition HITRAN has supplied a code that estimates the uncertainty of each halfwidth. Figure 2 displays these uncertainties for the water spectral lines between 500 and 14 000  $\text{cm}^{-1}$ . The error codes are values between 0 and 8. For clarity, each error code has had a value equal to the line position divided by 20 000 added to it. This merely spreads out the dots on the plot so that they are more visible. On the x axis are plotted the intensities of the spectral lines. One might expect that the uncertainties of stronger lines would be smaller than those of the weaker lines.

Error codes of 0, 1 and 2 indicate that the size of the uncertainty is unknown. A code of 3 indicates an uncertainty greater than 20%. The uncertainties become smaller (as indicated on the figure) as the code becomes larger until a code of 8 indicates an uncertainty of less than 1%. Most of the water lines have unknown uncertainties (error codes 0 and 2). Of those that do have known uncertainties, there is little relation between the uncertainty and the intensity of the spectral line. This is surprising since most often it is easier to measure the width of a stronger line. This strange situation is most likely a result of the very inhomogeneous nature of the widths in the database. The various spectral lines have been measured by many different groups and both the quality of the measurements and the means of reporting uncertainties are quite different.

Many atmospheric experiments now require accuracy in the 1 to 5% range. Not many of these

spectral lines meet that sort of criterion. A few years ago Bob Gamache did a study that showed that measurements of water lines that should have close to the same width (assuming vibrational invariance) actually varied by 15% from study to study. This brought into question the claimed uncertainties of all reported water halfwidths.

Figure 3 is similar to Figure 2 except that the points represent the carbon dioxide spectral lines on the HITRAN 2000 database. Other than a few weak lines, all of the uncertainties in the air broadened Lorentz halfwidths are listed in the 5 to 20% range. The halfwidths are based upon the measurements in a few bands performed in several laboratories and the assumption of vibrational invariance. The results from the best laboratories disagree by only about a percent and the variance between different vibrational levels is not much greater than that. The wide spread seen in the halfwidths of the water lines are not present here and the uncertainties are actually probably on the 1 or 2% level.

The uncertainties given in the HITRAN 2000 database are probably too conservative for CO<sub>2</sub>. There has been little attempt to upgrade these estimates because few seem to use this parameter. In fact, this parameter is potentially a very powerful tool for estimating uncertainties in atmospheric retrievals. It is not generally used in this manner both because this power is not always recognized and because the estimates are not very good. There is a circular logic here that has prevented the use of this tool.

Figure 4 is similar to Figures 2 and 3 except that the gas is methane. The uncertainty of the halfwidth of most lines is unknown. Some of the lines do have reported uncertainties and there does seem to be some correlation with intensity. The spectral lines with reported uncertainties come primarily from just a small number of studies which reported them. Those lines could be used to evaluate the contribution of the uncertainty of the air broadened halfwidth to the final product of an atmospheric experiment.

HITRAN currently only reports these uncertainties for the positions, intensities and air broadened halfwidths of the spectral lines on the list. The only way to evaluate the uncertainties of the other spectral line parameters is to reference the article from which the data were taken. Since there is no line by line reporting of the source of the data, one must search the HITRAN articles which report the changes from one edition of the database to the next. This is particularly difficult during the interval between the issuance of the database and the article documenting it. We are currently in that period for the HITRAN 2000.

While the Lorentz halfwidth of a spectral line is almost always important for atmospheric applications, the pressure shift is usually not. The definition of the pressure shift and the traditional means of measuring it are displayed in Figure 5. The position of the spectral line center at a given temperature is a linear function of pressure. Unlike the Lorentz halfwidth, we need two parameters to express the position as a function of pressure. The position at zero pressure is given in the HITRAN. This corresponds to the Lorentz width of zero at zero pressure. The slope of the line in the figure is the other parameter and is listed for each spectral line on the HITRAN also. As in Figure 1, the individual points in Figure 5 have different uncertainties associated with them since each is derived from an independent solution involving only one spectrum.

Generally, the positions of the spectral lines are better determined near zero pressure. There is less blending of spectral lines when the lines are narrowest. In addition, it is generally easier to find the center of a spectral line which is narrow. On the other hand, if the path length is not sufficient, the low pressure lines may not be intense enough for a good measurement of the position. The uncertainties of each point need to be somehow involved in the determination of the best line going through the points. In a later figure there will be more discussion of other things that can go wrong here as well.

While pressure shifts are not usually important in atmospheric measurements, this is not always the case. There are at least three types of exceptions. One is displayed in Figure 6 which comes from Curtis Rinsland of NASA Langley Research Center. The bottom panel displays a section of an ATMOS spectrum. The spectral line is P(24) of one of the CO<sub>2</sub> laser bands. This line has an unusual shape due to the fact that the solar radiation has passed through the atmosphere at many different altitudes (pressures). The broad wings are formed low in the atmosphere where the pressure is high while the central core is formed higher where the Lorentz width is smaller than the Doppler width.

The middle panel of Figure 6 displays the magnified residuals between the measured spectrum and what was calculated without the inclusion of a pressure shift. Systematic residuals well above the noise level are apparent. Soon after this fit was made, our group measured the pressure shift of this line and the top panel displays the magnified residuals between the observed spectrum and the newly calculated one. The improvement is dramatic. The remaining systematic residuals are comparable to the noise level.

Another situation in which the pressure shift may be important is where relief of saturation occurs. In Figure 6, the integrated absorption is pretty close even when the pressure shift is not included. For strongly absorbing lines with pressure shifts comparable to or greater than the Lorentz halfwidth, the peak of absorption at one altitude is separated in wavenumber from the absorption at another altitude by at least a quantity comparable to the halfwidth. This leaves more light for the strongest portion of the spectral line to absorb. A low resolution measurement (which is effectively just measuring the total absorption of the spectral line) then measures a stronger absorption than that simulated without a pressure shift. The mixing ratio of the atmospheric gas is then overestimated.

A third situation in which the pressure shift may be important is for correlation spectroscopy. If the position of the line is different in the atmosphere than it is in the correlation cell, the signal is reduced and the mixing ratio is underestimated.

How well can we measure these spectral line parameters from laboratory spectra? The answer to this question is often worse than it seems at first glance. Frequently, two groups measuring the same parameter will differ by several times either of their stated uncertainties. This is a long standing problem in molecular spectroscopy. What is its source?

Figures 7 and 8 will help explain one possible source of this problem. Figure 7a displays five laboratory spectra of the P6 manifold of the O<sub>3</sub> band of methane. Figure 7b displays the

magnified residuals after each spectrum is fitted for the best values of position, intensity and Lorentz width of each of the spectral lines and for the best values of some instrumental parameters such as continuum level. Each spectrum is fitted to its noise level, that is to about 0.1% in transmission. The spectral lines are all given Voigt profiles with the Doppler halfwidths set to that computed by theory. The fits are completely satisfactory.

The bottom panel of Figure 8 displays these same five spectra as well as 58 others in the region of the P11 manifold of the O<sub>3</sub> band of methane. This manifold was analyzed in the same manner as the P6 manifold. (Unfortunately, I do not have these two figures for the same manifold.) The resulting residuals from the parameters derived are displayed for all 63 spectra in the middle panel. The residuals are as large as 6% for a series of spectra with a noise level of 0.1%! Clearly, the spectral line parameters derived have not transferred well to the physical conditions of the other 58 spectra. This raises large doubts as to the usefulness for atmospheric simulations of the parameters derived. What has gone wrong? The laboratory spectra were fit to the noise level and the uncertainties were quite small.

Figure 7c helps answer this problem. The five spectra in Figure 7a have now been fitted in a single solution requiring consistent spectral line parameters from spectrum to spectrum. The number of free parameters is reduced from 120 to 47. Instead of fitting five intensities for each spectral line, only one is allowed. Instead of five spectral line positions for each line (to which a pressure shift is fit) only one position plus a pressure shift is fit for each spectral line. Instead of five Lorentz halfwidths, only one Lorentz halfwidth coefficient is fitted. The residuals from this fit are displayed in panel c. The quality of the fit is far worse than that in panel b and the residuals are much larger than the noise level.

What has gone wrong? In the single spectrum fits, there were enough free parameters to cover the inadequacies of the model used to calculate the spectrum. The resulting spectral line parameters were inconsistent from spectrum to spectrum. The simultaneous fit of all of the spectra reduced the number of free parameters enough to eliminate the overfitting. At the time that Figure 7 was made (1994), we had implemented a very approximate line mixing capability into the fitting technique. Figure 7d shows the residuals with 10 new parameters added for line mixing. Most of the residuals in panel c have been eliminated. Later refinement of the line mixing theory are displayed in the residuals shown in the top panel of Figure 8. While the middle panel of this figure shows something close to the best one can do with Voigt profiles, just a few additional line mixing parameters characterize the spectra to the noise level as displayed in the top panel.

Figure 9 adds an interesting sidelight to the fits in the O<sub>3</sub> band of methane with and without line mixing. This is a graph of the pressure shifts of the spectral lines of this band as a function of the quantum number  $m$ . The red dots are the values derived from the fits that did not include line mixing. The green squares are for the same lines in the fits that include line mixing. The differences are often about as large as the pressure shift itself! The first order affect of line mixing is to shift the spectral line proportional to pressure. These anomolous shifts are as large as the true pressure shifts. The pressure shifts from the first study were of no value to a theoretician who might decide to use these values to assist with his theory.

Are these line mixing effects large enough to significantly affect atmospheric measurements? Figure 10 displays the mean mixing ratio of methane for a day of measurements using a HALOE data set not including line mixing (the solid line on the left panel) and the same data set with the approximate line mixing formulation (the dotted line on the left panel). The atmospheric data are from the methane channel of the HALOE experiment, a gas correlation instrument that uses the sun as a source in occultation mode. The methane channel is located in the P branch of the  $O_3$  band of methane. The percentage difference is displayed in the right panel. At altitudes between 0.1 and a few millibars, the line mixing reduces the mixing ratio of methane by about 2 or 3%. At altitudes below 10 millibars the mixing ratio of methane is increased by more and more until it reaches about 15% at 200 or 300 millibars. For the atmospheric scientist, these differences are significant.

Line mixing only affects the Lorentz profile of the spectral line. Thus, there should be little effect at high altitudes (low pressures). Why does the effect of line mixing not disappear at high altitudes in these data? HALOE is a gas correlation spectrometer that uses an internal correlation cell with about 600 millibars of pressure. The effect of the line mixing in the cell is the source of the differences at higher altitudes.

These errors can propagate in an atmospheric retrieval and can be important in the compensation for interfering spectral lines. The HALOE HCl channel is also located in the P branch of the  $O_3$  band of methane. Inversion of the HALOE data requires compensation for the interfering methane lines which have line mixing. In addition, the inversion uses the results of the methane channel to set the mixing ratio of the interfering gas. Mean mixing ratio profiles for a day of HALOE data are displayed in Figure 11 in the same format as the methane is displayed in Figure 10. Differences of as much as a few percent are seen when the line mixing is included.

Am I being honest at this point or have I chosen a case to most exaggerate my case? Figure 12 displays all of the HALOE methane channel data for about a month. The vertical axis is height in the atmosphere (pressure level in millibars) and the horizontal axis is latitude in degrees. Color indicates the percentage change caused by the inclusion of line mixing in the inversions. Hundreds of individual profiles contributed to this figure. High in the atmosphere, the change is about 2%, independent of latitude. Below 20 millibars or so the change is always greater than 5%.

Figure 13 is equivalent to Figure 12 for the HCl channel of HALOE. The effects above the 100 millibar level are mostly at the 2% level or so, but the line mixing does make a considerable difference in the stratosphere of high southern latitudes.

If an effect such as line mixing might be important for atmospheric measurements, might there be other spectroscopic effects that are currently neglected which are also important in some cases? At the 1% precision level, Dicke narrowing is almost important. Any pushes to better precision will require its inclusion. Speed dependant profiles may also be important at some level. While our group has not included this effect in any of our measurements, other groups have reported that it is measureable in laboratory spectra. As precisions in atmospheric measurement are pressed farther, this effect will probably also become important.

At this point let us turn to the topic of how well spectral line parameters may be measured in the laboratory today. The lower panel of Figure 14 displays two simulated spectral lines. These are at high enough pressure that Lorentz broadening is dominating over Doppler broadening. The only difference between the two spectra is a 1% difference in the Lorentz halfwidth coefficient. The depth of the spectral line is about 8%, so it is relatively free of saturation effects. The maximum difference between the two curves is less than 0.08% in transmission. Thus, for the best single point in a spectrum the difference between these lines requires a signal to noise ratio of better than 1000 to tell the two spectra apart. This level is achievable today, but as the requirements for better spectral line parameters become more rigid, this will become a problem. To achieve an accuracy of the order of 0.1% would require a signal to noise level of better than 10 000. Fitting the spectrum actually requires somewhat less signal to noise than this since several points contribute information on the Lorentz halfwidth coefficient. The relaxation of the signal to noise requirement is not very great, though.

Figure 15 again plots two nearly identical spectra. Now the pressure is low enough that the Doppler profile is dominating the Lorentz profile. The spectral line is relatively weak, but the area under the line should be quite independent of the Lorentz halfwidth. This is an attractive situation since the area under the line is, for many spectrometers, independent of the resolution or line profile. The difference between the two profiles is 1% in the spectral line intensity. In order to get the difference to the level of the RMS noise level would require a spectrum with a signal to noise of 4000. This is achievable, but pushing to more stringent requirements soon starts straining the experimenters.

Figure 16 displays the problems that can be induced by lack of knowledge of the instrumental line shape. The two plotted spectral lines differ in several ways. In one spectrum an FTS phase error is introduced and the continuum level is misrepresented by 0.01%. The intensity of the spectral line is 1% different and the position different by  $0.000\ 05\ \text{cm}^{-1}$ . This level of phase error is small enough to likely escape scrutiny by eye. In order to detect this 1% error in intensity requires a signal to noise ratio of better than 2000. To push measurement to more accurate levels would be difficult. The lesson is that the spectrometer must be well understood.

Figure 17 illustrates another instrumental problem that can affect the measurement of spectral line intensities. Here the two lines plotted differ in two ways. One has a misrecognized zero level by 1%. The intensity of the spectral line is different in the two spectra by 1%. Seeing the difference between these profiles requires a signal to noise of 50 000. Notice how closely the difference resembles the spectrum. If I had been more careful in choosing the difference in intensity between the two spectral line calculations, the difference could have been smaller by perhaps an order of magnitude. Almost all spectrometers have problems with zero level offsets. There is always the problem of stray light, but a Fourier transform spectrometer may also introduce an offset due to detector nonlinearity and a diode laser spectrometer might have a small amount of undetected mixed mode. The error in intensity derived is always at least as large as the misplacement of the zero level.

The point of this talk is to review spectral line parameters other than position and intensity. Why has so much emphasis placed upon intensity in the previous figures? Figure 18 explains why. Here two spectral lines are again displayed. The difference is that the second calculation is for a

line that has an intensity 1% larger and a Lorentz halfwidth 1% smaller than the first line. The lines are saturated and should contain a great deal of information concerning the Lorentz halfwidth since the wings have enough intensity to measure their shape well. The difference between these curves is quite small. In order to see the difference requires a signal to noise of about 200 000. In order to measure the Lorentz halfwidth of a saturated spectral line requires independent information concerning the intensity. The Lorentz halfwidth and the intensity are strongly anticorrelated in saturated lines. The issue of determining intensities to a given level must be solved before halfwidths can be determined to the same level. The only alternative is to measure unsaturated lines. For these the wings are more difficult to measure and the measurements are more sensitive to instrumental effects such as the placement of the zero level and the continuum. In order to measure a Lorentz halfwidth well, a method is required to break the strong anticorrelation between the intensity and Lorentz halfwidth. The wings of these strong lines then provide a great deal of information.

Figures 19 to 22 are another means of seeing how this problem influences measurement of spectra and the means of overcoming this problem. The spectrum fits involved in the creation of these figures are of the R2 manifold of the O<sub>3</sub> methane band. The resolution is 0.01 cm<sup>-1</sup> and there are two spectral lines separated by only 0.01 cm<sup>-1</sup>. This means that not only are the intensity and Lorentz halfwidth of each spectral line highly anticorrelated with one another, but at any significant pressure the two lines are strongly blended. The two intensities and the two Lorentz widths are each strongly correlated or anticorrelated with all of the other three. For the spectrum in Figure 19, the pressure is 500 Torr. This means that the Lorentz halfwidth is a few times larger than the separation of the spectral lines and the lines are completely blended. This figure investigates the anticorrelation between the two Lorentz halfwidth coefficients. For each point on the figure, the two Lorentz halfwidth coefficients are fixed to the values specified on the two axes. The solution is then allowed to converge with all of the other spectral line parameters and instrumental parameters free until the sum of the squares of the residuals is minimized. Color represents a value that is proportional to the minimized sum of squares. The minimum corresponds to a point near the lower right corner of the figure. This means that the best Lorentz halfwidth coefficient for the spectral line at 3038.61 cm<sup>-1</sup> is about 0.06 cm<sup>-1</sup>/atm and the best Lorentz halfwidth coefficient for the spectral line at 3038.62 cm<sup>-1</sup> is about 0.10 cm<sup>-1</sup>/atm. The blue area stretching from the lower right to upper left represents the anticorrelation of these two parameters. But is this really the correct value? The spectral lines are not resolved.

Perhaps a better measure would be possible with somewhat lower pressure. Figure 20 is the same as Figure 19 except that the spectrum fitted has only 100 Torr pressure. The Lorentz halfwidths here are close to 0.01 cm<sup>-1</sup>. The separation of the lines and the instrumental resolution are close to this same value, so the lines are starting to get close to being resolved. On the other hand, the lower pressure reduces the amount of Lorentz halfwidth information available in the spectrum. The results are surprising. The best values of the two Lorentz halfwidth coefficients are at the lower left corner of the figure. The best value for each Lorentz halfwidth coefficient is between 0.06 and 0.07 cm<sup>-1</sup>/atm. One line has close to the same halfwidth coefficient derived from both spectra (as it should), but the other line has quite different values. There is clearly something wrong. Is there another test that can be tried?

Perhaps trying to analyze a spectrum in which the two lines are resolved will give an answer to

the dilemma of what the best values of the Lorentz halfwidth coefficient. Figure 21 is of the same form as Figures 19 and 20 except that the spectrum is now one of the gas at a pressure of only one Torr. The lines are now resolved, though not completely. The Doppler width is greater than the Lorentz width, but is less than the resolution of the spectrometer. With the lines now mostly separated, the width and intensity information of the two lines should be separated. Unfortunately, though, Figure 21 shows that the Lorentz halfwidth coefficient information in this spectrum is nil. The problem is that when there is halfwidth information, there is always correlation between the spectral line parameters of the two lines. When the correlation is removed, there is no halfwidth information. Somehow the uncorrelated information of the low pressure case must be used to constrain the solution for those cases where there is halfwidth information.

The solution to this problem is to fit all three spectra simultaneously. The one Torr spectrum provides uncorrelated information concerning position and intensity of each of the two spectral lines. The higher pressure spectra have a great deal of halfwidth information and this information is released by the constraints to the positions and intensities provided by the low pressure spectrum. The solution with all three spectra is displayed in Figure 22 in the same manner as Figures 19 to 21. There is now a clear bullseye pattern that defines the Lorentz halfwidth coefficients well. The surprising part is that the answer does not correspond to what was derived in any of the other solutions. One of the halfwidth coefficients is between  $0.06$  and  $0.07\text{ cm}^{-1}/\text{atm}$  and the other is between  $0.08$  and  $0.09\text{ cm}^{-1}/\text{atm}$ . The bullseye is not elongated either from upper left to lower right (anticorrelation) nor from lower left to upper right (correlation). The elongation in the horizontal direction indicates that the Lorentz halfwidth coefficient of the  $3038.62\text{ cm}^{-1}$  line is more uncertain than that for the line at  $3038.61\text{ cm}^{-1}$ .

The lesson is that the best information can be derived only from a solution which includes all the information available. This can only be done with single spectrum analysis if the individual solutions are combined using the full correlation matrices. The more straightforward manner (and completely equivalent) is to simply include all of the spectra in a single solution.

This technique is not limited to simple spectra. Figure 23 is from Malathy's poster presentation. The figure contains only a portion of the fitted region. The fit contains both self and air broadened spectra and both natural isotope mixtures and rare isotope enhanced mixtures. The continuum and zero levels of each spectrum must be determined separately, but the spectral line parameters are required to be consistent from spectrum to spectrum.

Vibration-rotation bands are best investigated in their entirety. In particular, the continuum and zero levels need to be characterized in a consistent manner, that is, without discontinuities between small fitted intervals. In Figure 24 (taken from Malathy's poster presentation)  $100\text{ cm}^{-1}$  is fitted in order to cover an entire laser band of carbon dioxide. There are 22 spectra in the solution and the residuals are all at the noise level of the spectra. In order to achieve this, it is essential to characterize the instrumental line shape, wavenumber scale and physical conditions of the spectra very well. The instrumental line shape is best studied with unresolved spectral lines. The wavenumber scale must be known to a precision at least as good as the precision of the best measured spectral line position. The absolute wavenumber scale need not meet this criterion, only the precision from spectrum to spectrum. These are Fourier transform spectra and



the wavenumber scale provided by the Fourier transform generally fails to be good enough by an order of magnitude or two. It is best to align the wavenumber scales using spectral lines that are narrow and are formed from a part of the path of the beam where the pressure is the same in each spectrum in order to avoid errors due to pressure shifts. The physical conditions as recorded by the experimentalist are rarely precise enough for a fit such as this. The precision of the gas amount from spectrum to spectrum must be almost 0.1%. Knowing pressures and mixing ratios to this level from pressure gauges is difficult and it is necessary to vary the amount of gas in each spectrum within its experimental uncertainty until the residuals are reduced to the noise level. The reduction of the residuals to the noise level as in Figure 24 indicates that all of these “calibrations” have been done as well as can be done and that the model for the spectral line shape is adequate for the information content of the spectra.

Figure 25 (again from Malathy’s poster presentation) is a fit of the same 22 spectra as Figure 24. This region of about  $70\text{ cm}^{-1}$  includes almost all of another of the laser bands of carbon dioxide. Here there is a slight systematic in the residuals which indicates that something of the calibration or instrumental line shape was slightly inadequate for the information contained in the spectra. It is only through this sort of fit that one can be completely sure of some of the nonvoigt line shapes. When the spectrum is fitted one spectral line at a time, much is lost in the wings of the line due to overfitting of the continuum, zero level and other such instrumental effects. These same wings often contain most of the information on line shape.

Figure 26 illustrates the fact that the spectrum need not be simple in order to do a multispectrum fit. The figure displays a fit of 50 spectra in the spectral region of the P7 manifold of the  $\text{O}_3$  band of methane. Unfortunately, the P6 manifold of the same band in the  $^{13}\text{CH}_4$  isotopomer falls right on top of this manifold. The two isotopomer spectra are so highly blended that it is impossible to extract the spectral line parameters very well for either isotopomer. This solution solves that problem by having spectra with both a natural mixture of isotopomers (99%  $^{12}\text{CH}_4$ ) as well as spectra with predominantly  $^{13}\text{CH}_4$ . While no one spectrum clearly separates the two isotopomers, the two are nicely separated by inclusion of both types of spectra in the multispectrum solution. This fit also contains both air broadened and self broadened spectra, low temperature ( $-60^\circ\text{C}$  to room temperature) air broadened spectra and spectra with primarily the  $^{12}\text{CH}_3\text{D}$  isotopomer. Line mixing is strong within the manifold. Positions, intensities, self and air induced pressure shift coefficients and temperature dependance of the air induced shift, self and air Lorentz broadening coefficients and the temperature dependance of the air broadening and off diagonal relaxation matrix element coefficients for both air and self broadening and the temperature dependance of this parameter for air broadening are all retrievable for at least some of the spectral lines. Figure 27 displays in table form some of the statistics of this fit. There are on the order of  $10^5$  fitted points which are used to determine 961 free parameters. The computation time has improved since this figure was made (due to both algorithm and computer enhancements) to about 1 minute per iteration.

Figure 28 summarizes the advantages of the multispectrum fitting technique.

Intensities and Lorentz widths of spectral lines are now routinely measured to a few percent from laboratory spectra. In many cases this accuracy approaches 1%. Unfortunately, comparison of measurements from different laboratories often differ by considerably more than the quoted

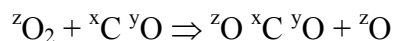
uncertainties. The classic case of this was the paper written concerning the Lorentz broadened halfwidth coefficientss of water by Bob Gamache several years ago. While many laboratories claimed accuracy of a few percent or better, Gamache found fundamental disagreements of 15% between laboratories. From where do these systematic differences arise? Is it possible to push accuracies of spectral lines to an order of magnitude better? Figure 29 is a list of eight experimental problems which limit accuracy of spectral line parameters to the current level.

**Pressure guages** are trusted too much. While many pressure guages are quoted as accurate to 0.1% of full scale (or better), one must treat these numbers with some suspicion. Guages need frequent calibration. Furthermore, as discussed below, one must question just what the guage is measuring.

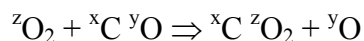
How long is the path length in the cell? Most experiments use a **converging beam** through the cell. As a result, different parts of the beam have different path lengths. The errors induced by this effect are generally too small to be of concern when measuring at the 1% level, but in some cases will be important before reaching the 0.1% level. In order to avoid this problem, one might try to put parallel light through the cell. This often creates problems with internal reflections (**etaloning**). Part of the beam passes through the gas 3 times (or 5, 7, etc.) rather than once and one must account for interference between the beams with different path lengths. If only 1% of the light has undergone three passes, the mean path length has changed by 2%. Keeping the etaloning below this level is quite possible as long as the cell is long enough, but this effect must be considered much more often if accuracies an order of magnitude better are required.

Precise **calibration of the frequency scale** is required to make the multispectrum technique work. In addition, this calibration is required in almost any type of analysis in order to measure pressure shifts. Any improvements in positions or pressure shifts would require an equal improvement here.

An often overlooked source of error is the **isotopomer mixing ratios** in the gas sample. For example, a typical cylinder of carbon dioxide purchased from a commercial source contains a mixing ratio of  $^{13}\text{C}$  about 3% different than the carbon dioxide in the atmosphere. This is because the commercial gas is produced from fossil fuel sources. Correction of such an effect is not too difficult at the 1% level as long as one is aware of the problem. Correction at the 0.1% level, however, is much more difficult. The particular sample placed in the cell must be measured for the isotopomer (not isotopic) mixing ratios to quite stringent levels. It is not even safe to assume that the isotopomers are in equilibrium. For example, commercial carbon dioxide enriched in the rarer isotopes is often made by passing CO enriched in the rarer isotopes and  $\text{O}_2$  with a natural mixture of isotopes over a catalyst. There are two possible chemical reactions to create the carbon dioxide. The first breaks the bond of the  $\text{O}_2$  and places the O atom into the CO molecule.



The second breaks the bond of the CO molecule and attaches the  $\text{O}_2$  to the carbon atom.



The resulting mixing ratios of isotopomers is quite different and neither is the equilibrium mixture. Resolution of the mixing ratios of the various isotopomers is essential to measurement of the absolute intensities of the spectral lines of each isotopomer. This is much less a problem at the level of measurement of 1% in intensity and Lorentz width than it is at the 0.1% level.

**Mixing of gases** often occurs much more slowly than is anticipated. This affects final results in two manners. If the gas lines feeding the absorption cell have a volume that is a significant fraction of that of the cell and/or if the beam passes through much less than all of the gas in the cell, the abundance (mass path) of the absorbing gas in the beam may be significantly different from that of the mean of all gas let out of the gas bottles. Secondly, the mixing ratio seen by an absorbing molecule will not necessarily be that of the cell as a whole. In particular, more molecules of the absorbing gas will find themselves in a section of the absorption cell where there is more self broadening (and shifting and line mixing, etc.) than average. This problem is likely to become much more difficult as a push to greater accuracy than 1% is required.

Passivation of the absorption cell and the gas handling system is another source of error. Firstly, this can introduce the problem of changing gas amount during the time that the spectrum is being recorded. Secondly, **outgassing** of other molecules (**especially water**) that are adsorbed onto the walls of the cell and the gas handling system may dilute the gas mixture. This is a particularly difficult problem for low pressure spectra. A pressure of 1 Torr only requires an outgassing of 10 microns of another gas to change the amount of absorbing gas by 1% from the pressure gauge reading. Very good vacuums are required to remove this sort of contamination especially if there is a push toward the 0.1% accuracy level. The best way around this problem (besides good vacuums and good passivation) is to be sure that there are spectra in the solution for which the amount of absorbing gas is well known. The low pressure spectra abundances can then be adjusted to force agreement between spectra.

Finally, 1% accuracy is achievable for intensities and Lorentz halfwidth coefficients if knowledge of the **temperature and temperature uniformity** in the cell are at the about one degree Kelvin level (at room temperature.) Such uniformity becomes difficult when temperatures far from room temperature are required, but is possible. Pushing this uniformity requirement an order of magnitude for anything but a small cell is much more difficult.

In conclusion, absolute measurement of Lorentz halfwidths today are, at best, good to something of the order of 1%. Significant improvement will require work in many directions - there is no one (or few) problem(s) that limit accuracy now. The multispectrum technique allows for precisions to a level of 0.1% or a bit larger by removing a lot of the correlation problems and overfitting problems. Better halfwidths are not meaningful for many gases unless the spectral line model is improved over the Voigt model. Effects such as Dicke narrowing, line mixing and speed dependant profiles become important at the sub 1% level. Finally, careful measurement and understanding of physical conditions in the laboratory are essential.

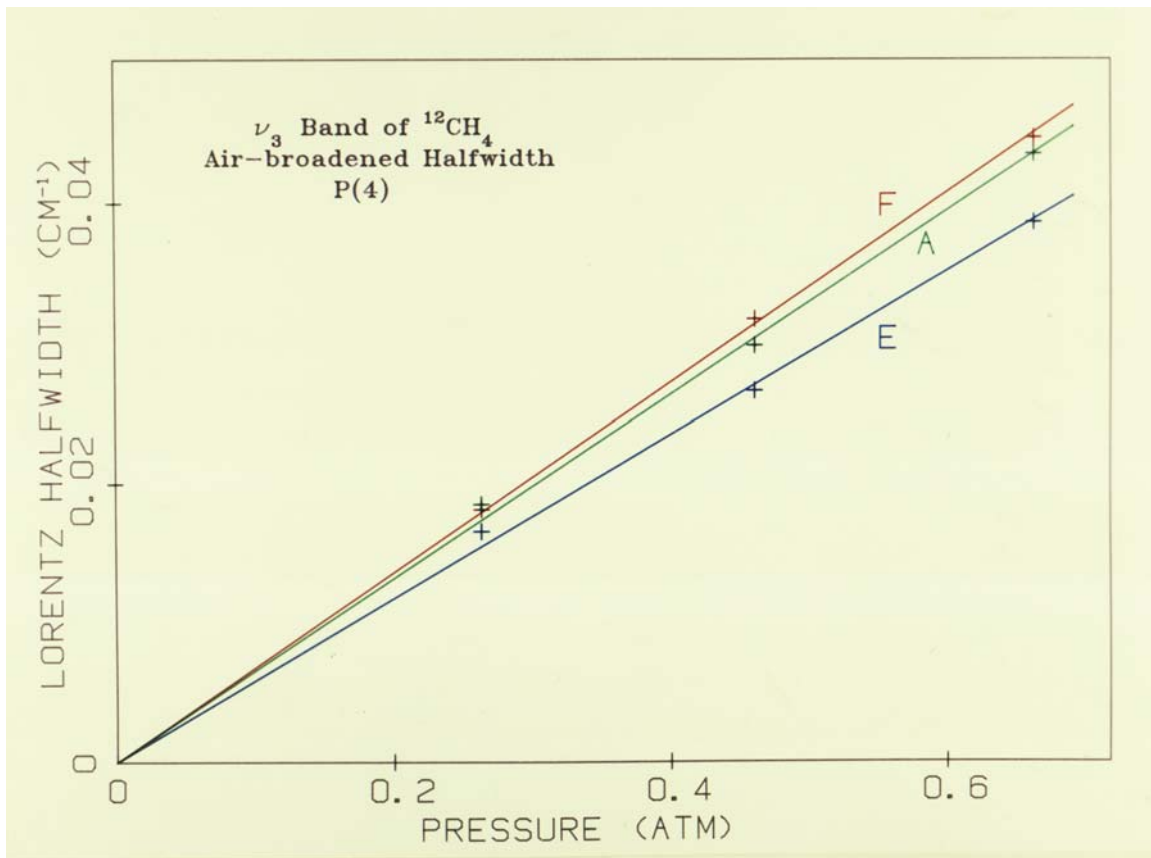


Figure 1

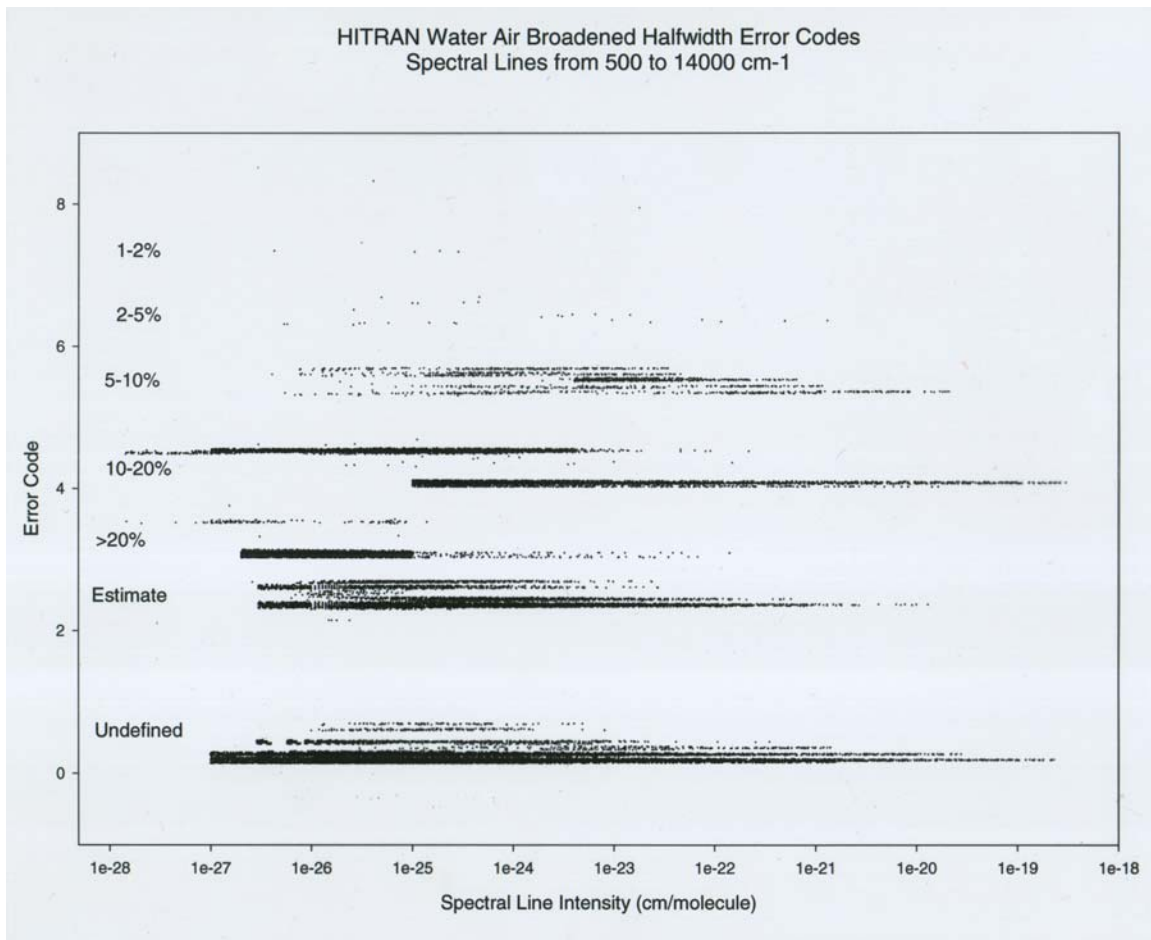


Figure 2

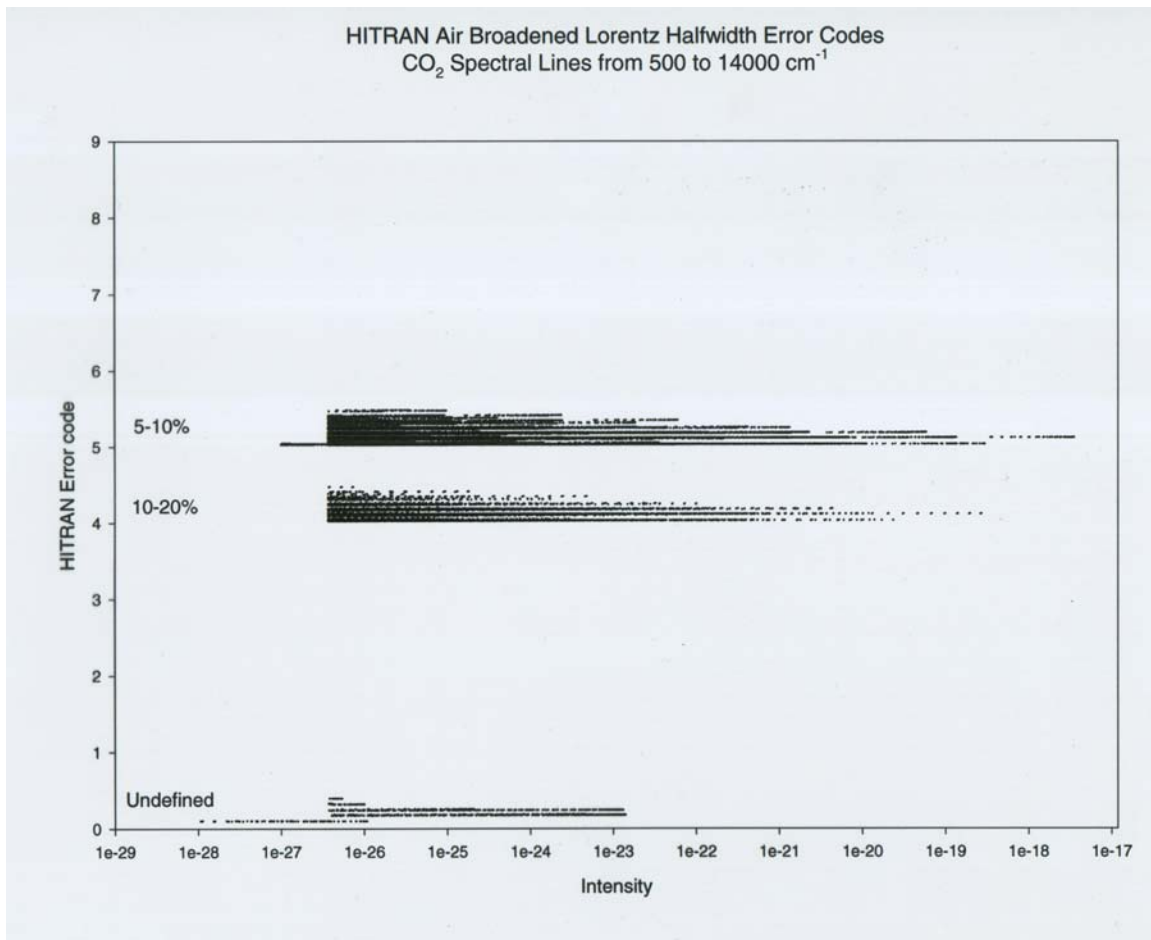


Figure 3

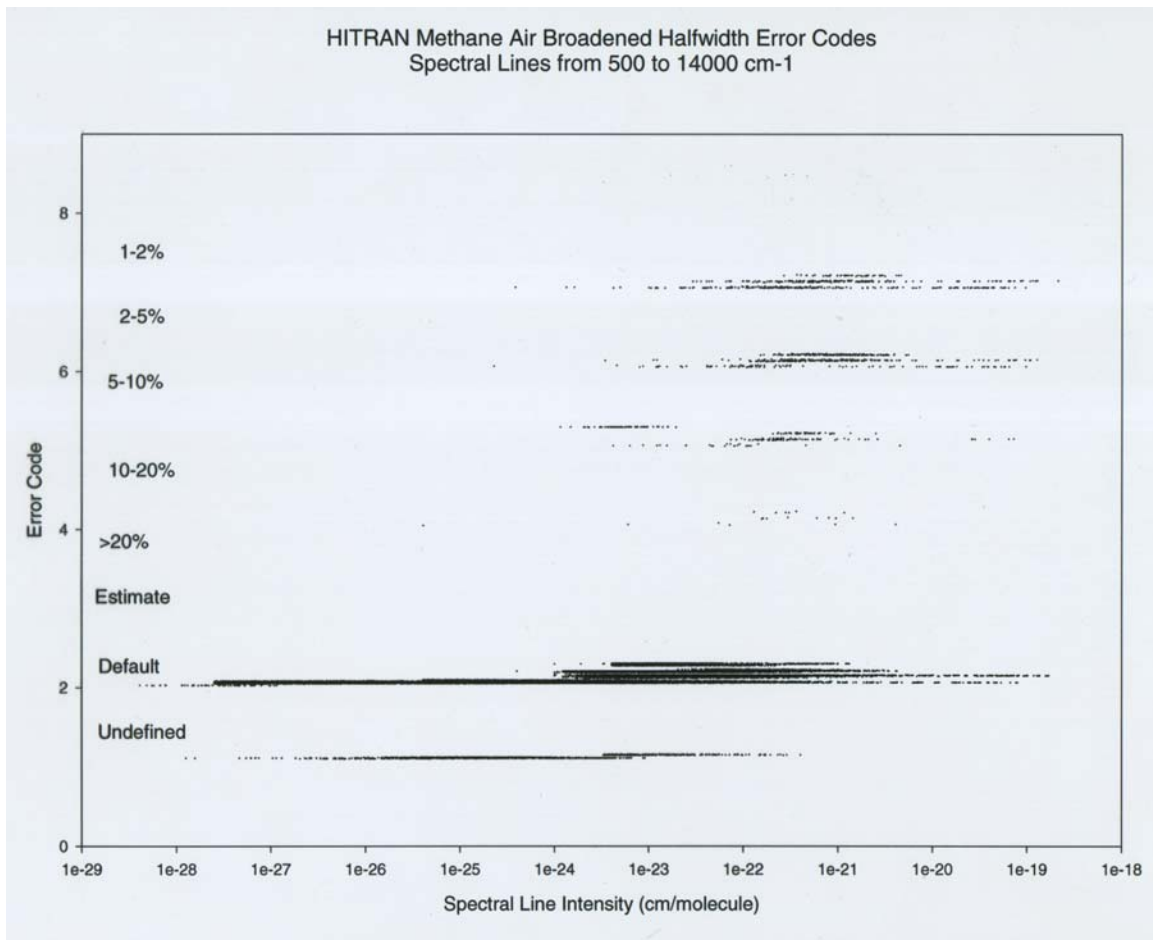


Figure 4

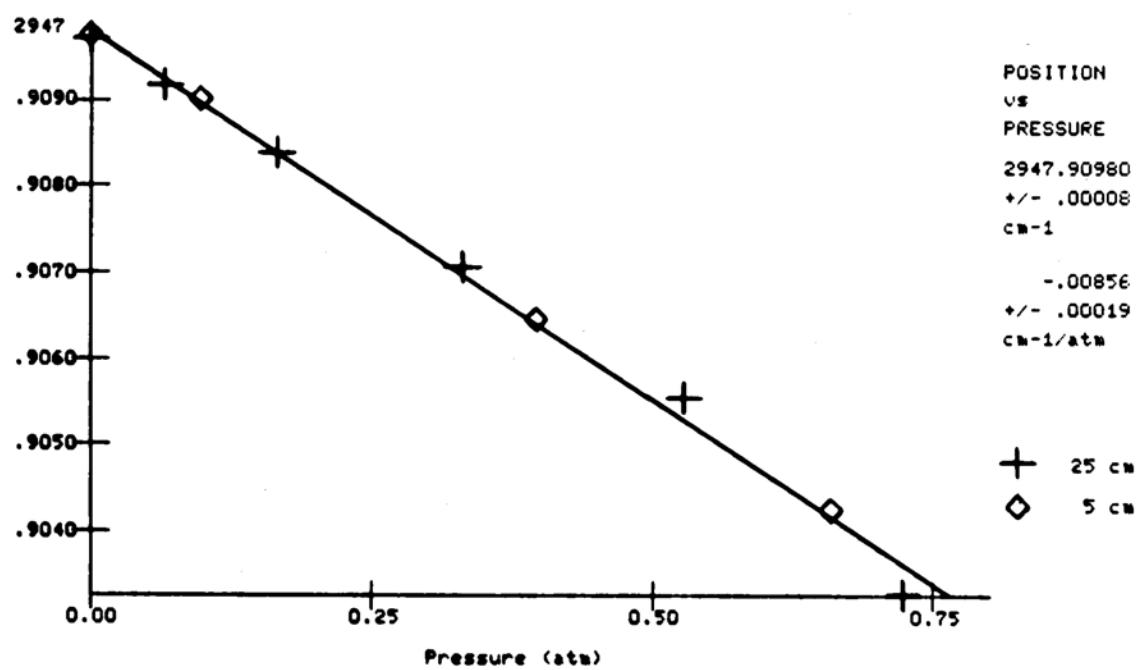


Figure 5



CO<sub>2</sub> LASER BAND LINE  
IN ATMOSPHERIC SPECTRUM TAKEN AT KITT PEAK

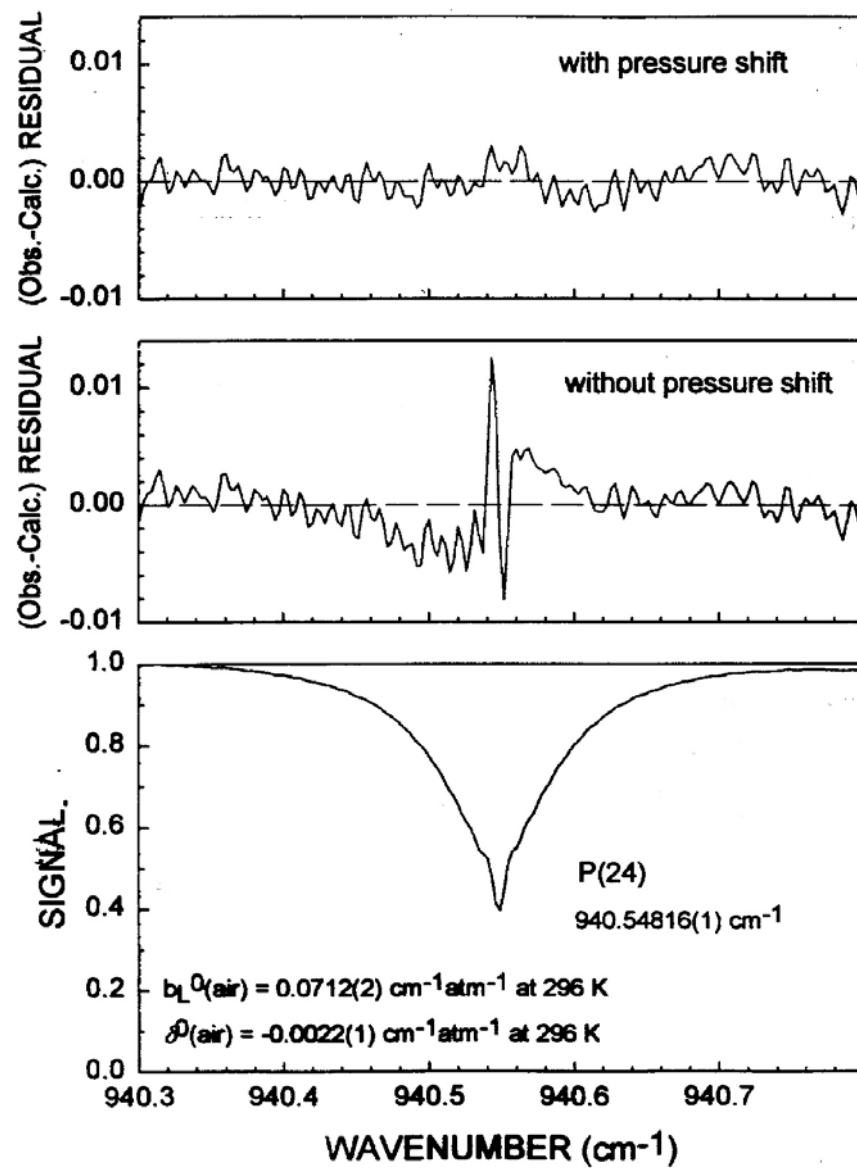


Figure 6

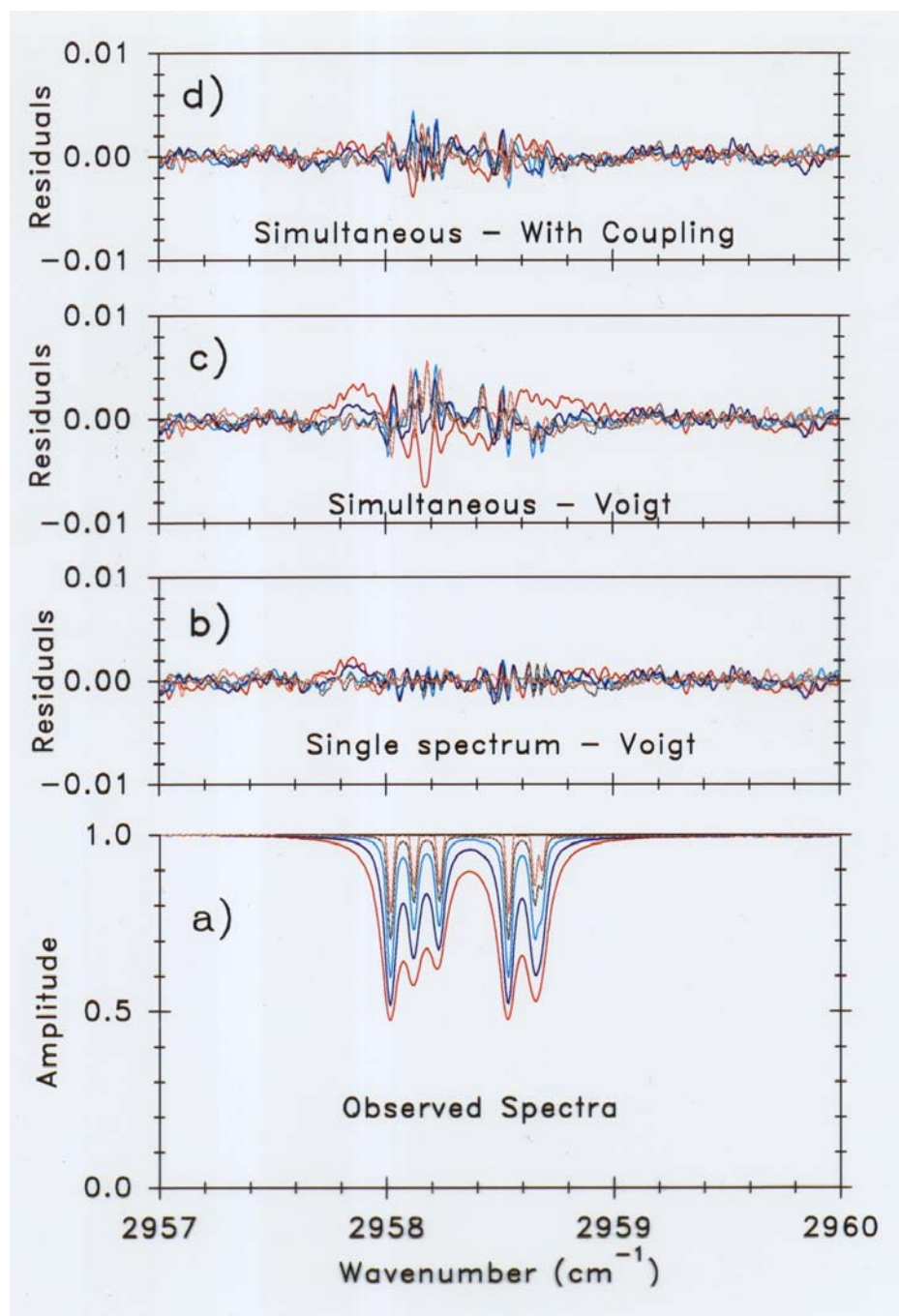


Figure 7

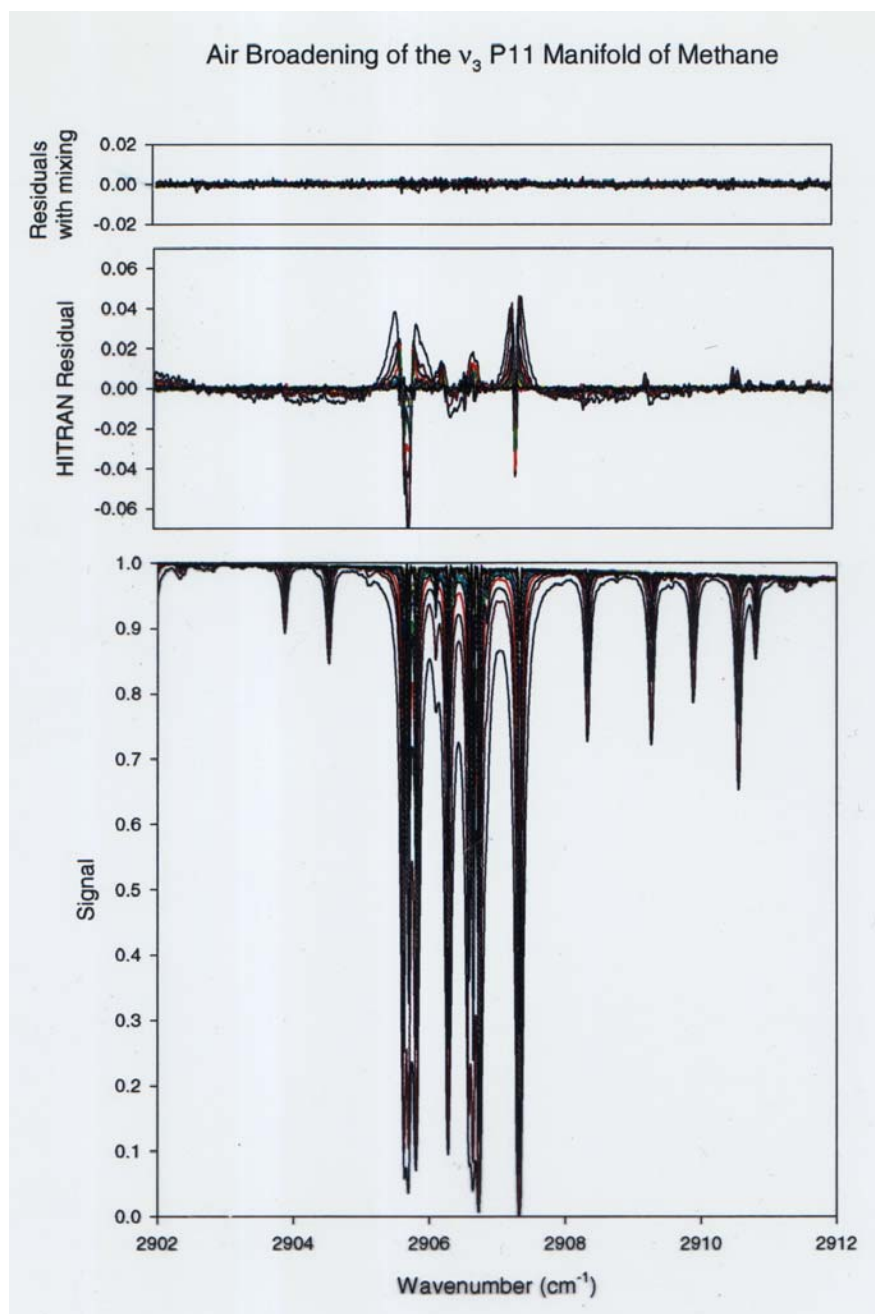


Figure 8

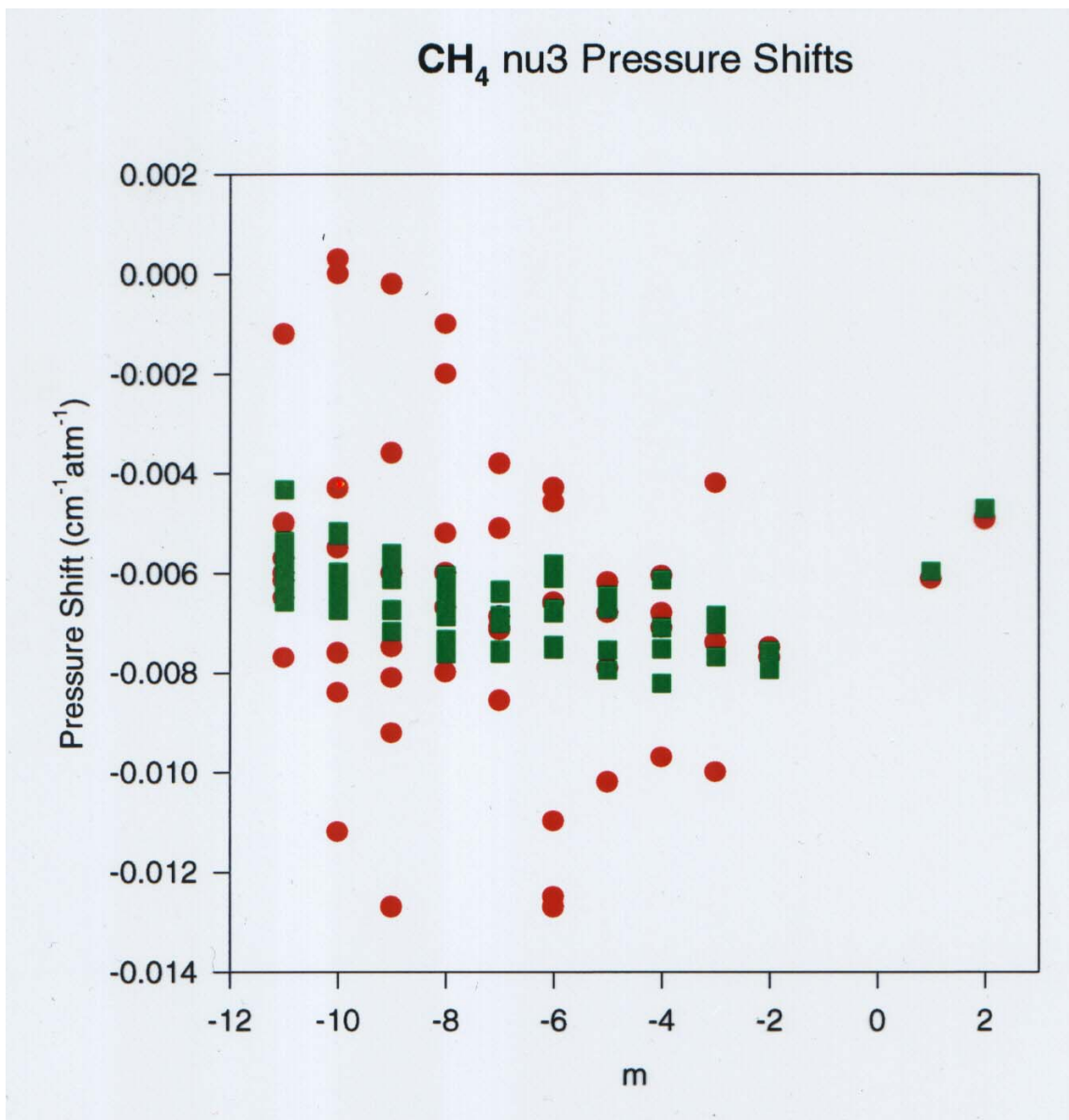
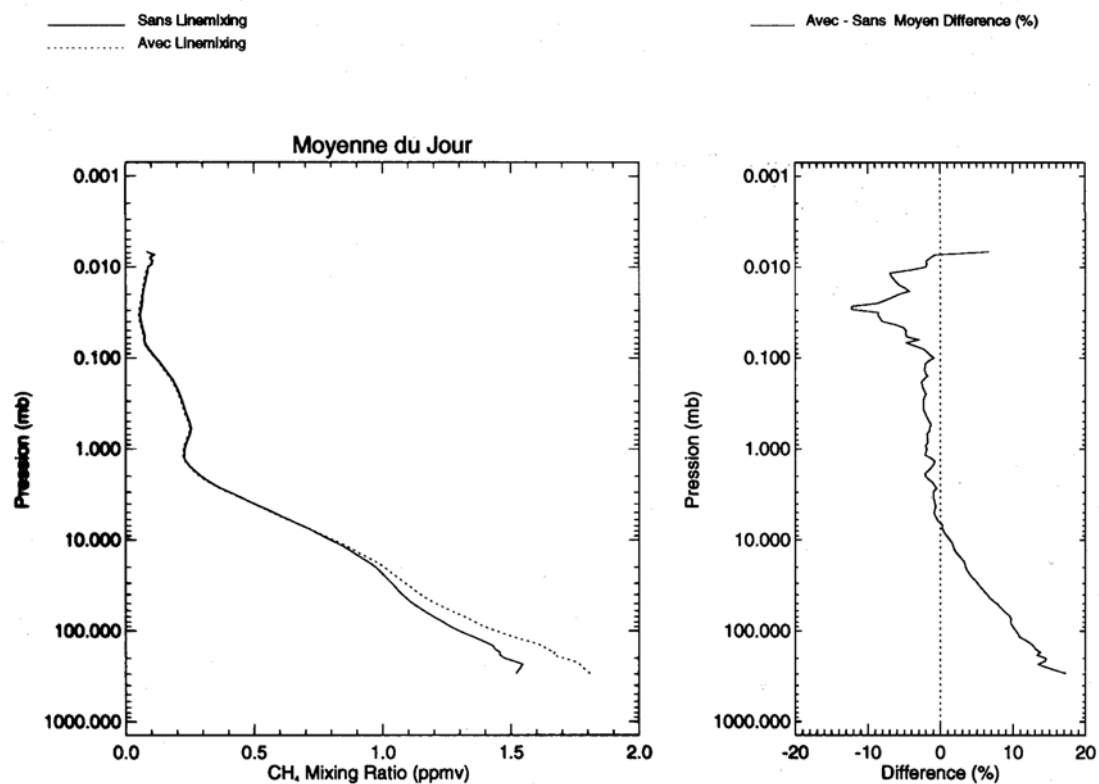


Figure 9



**HALOE CH<sub>4</sub> 24-Avr-1994 Lever du Soleil Proche de 54 S  
Avec et Sans Linemixing**

Wed Oct 7 15:12:02 GDT 1998

Figure 10

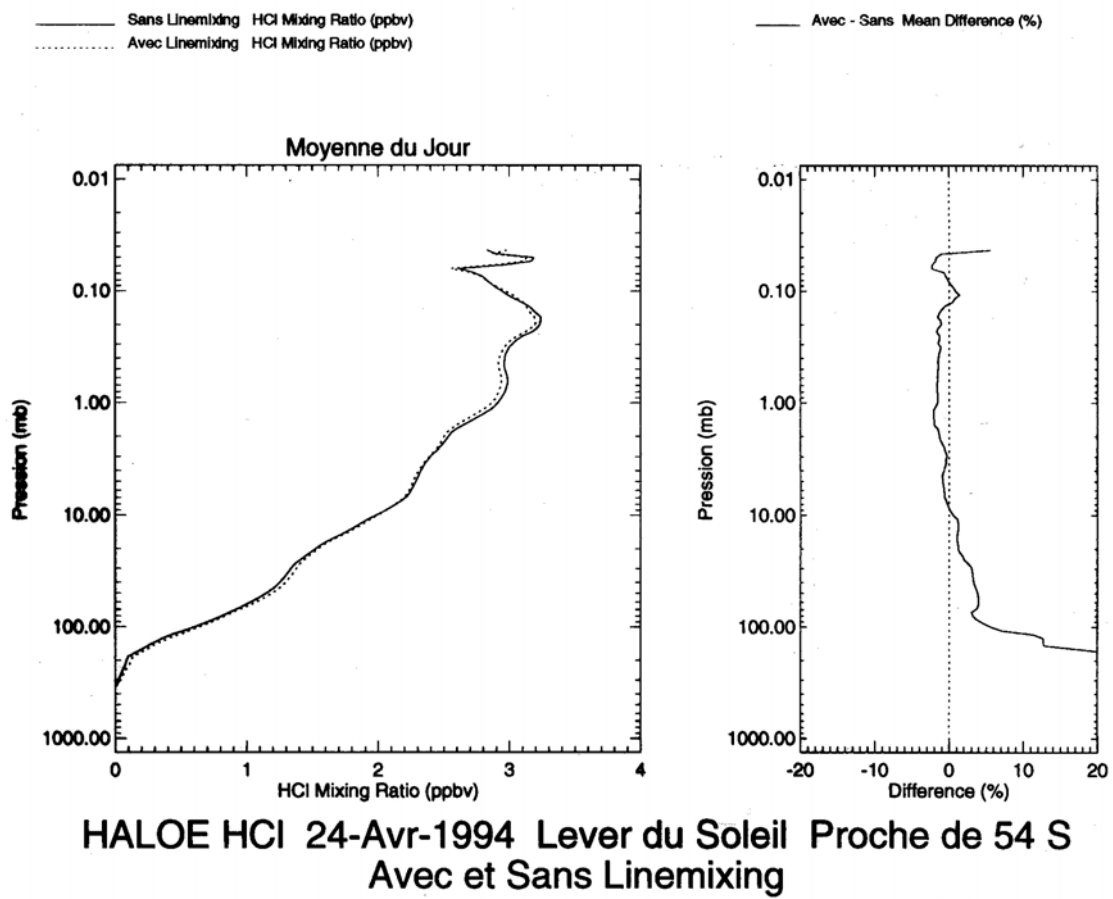


Figure 11

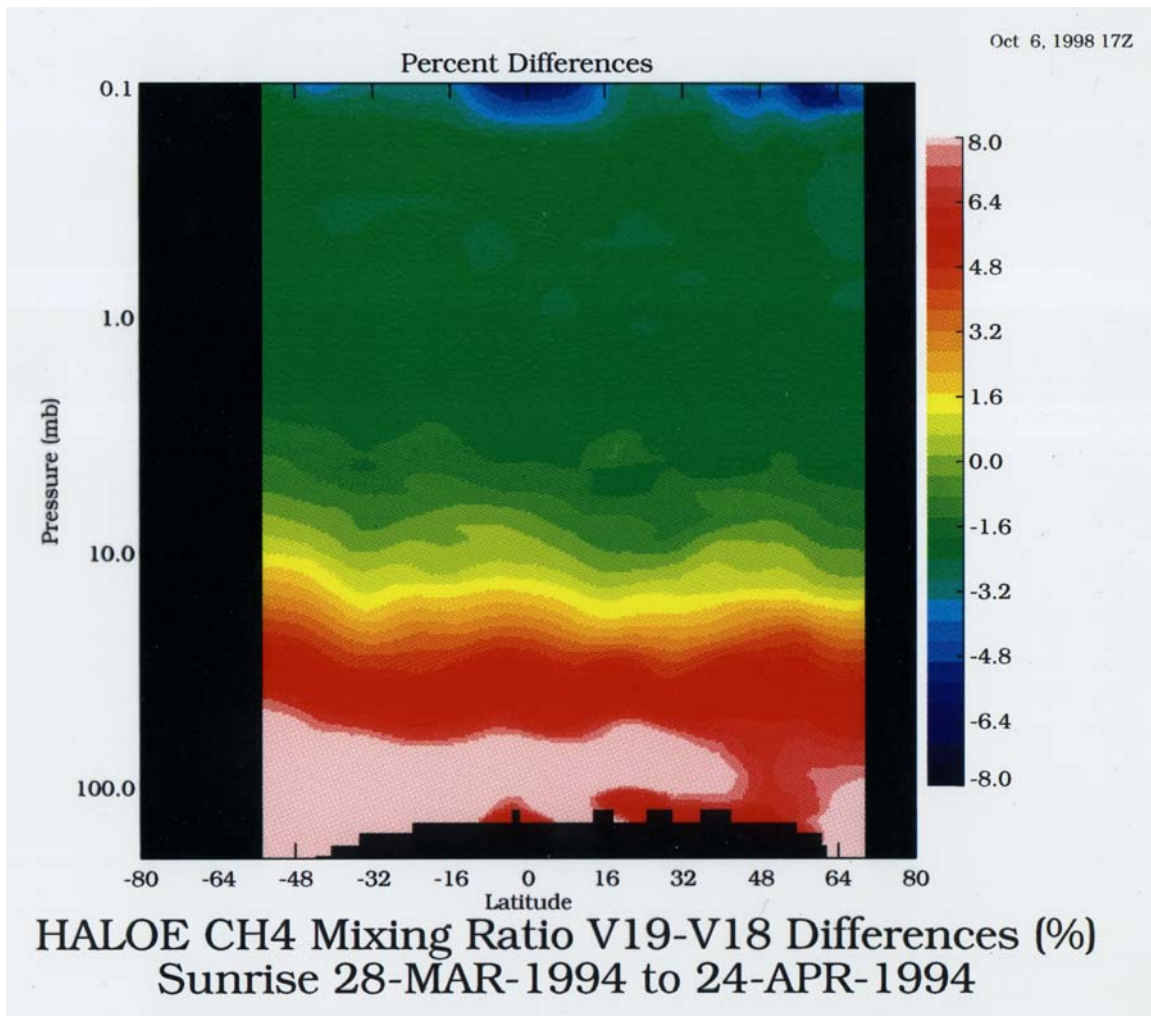


Figure 12

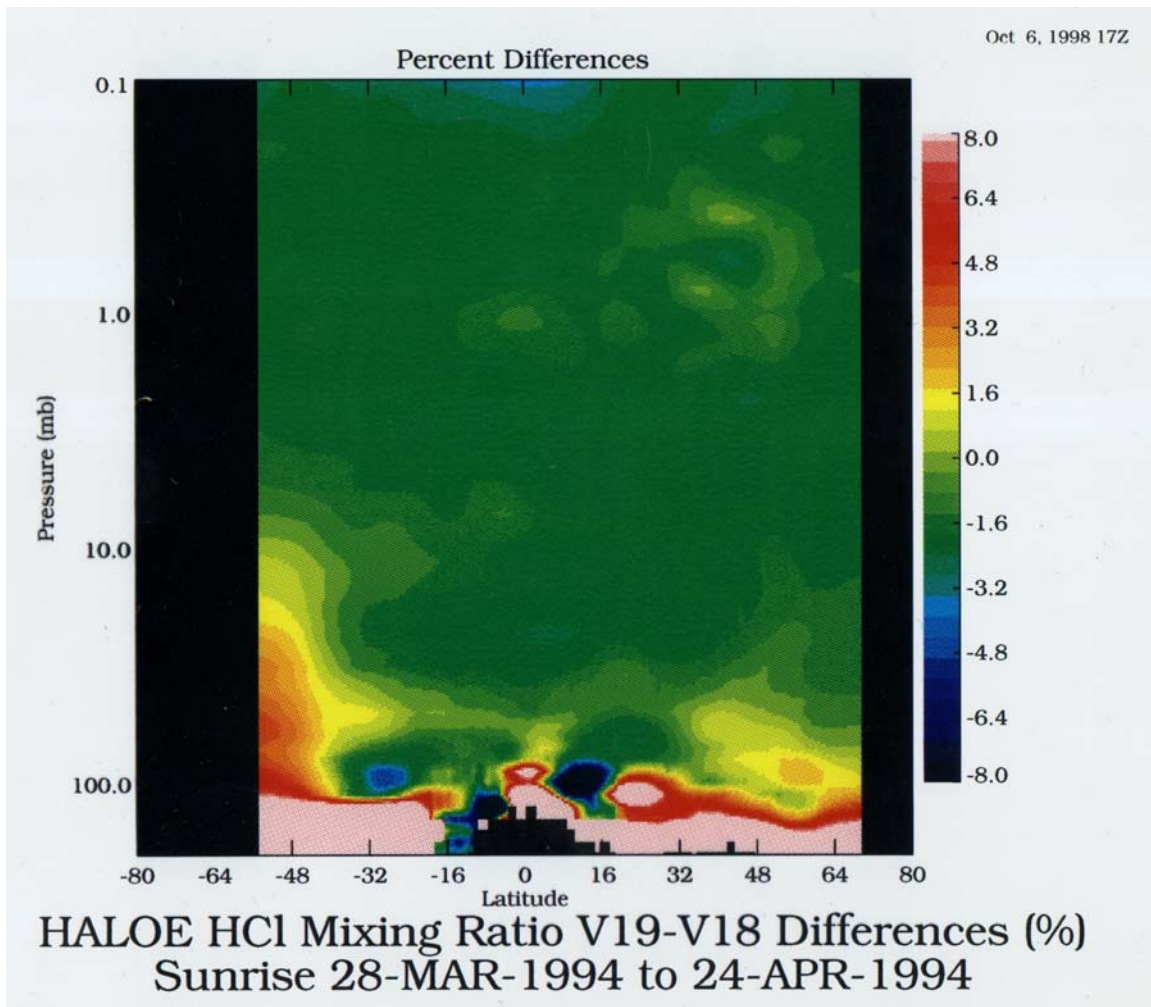


Figure 13



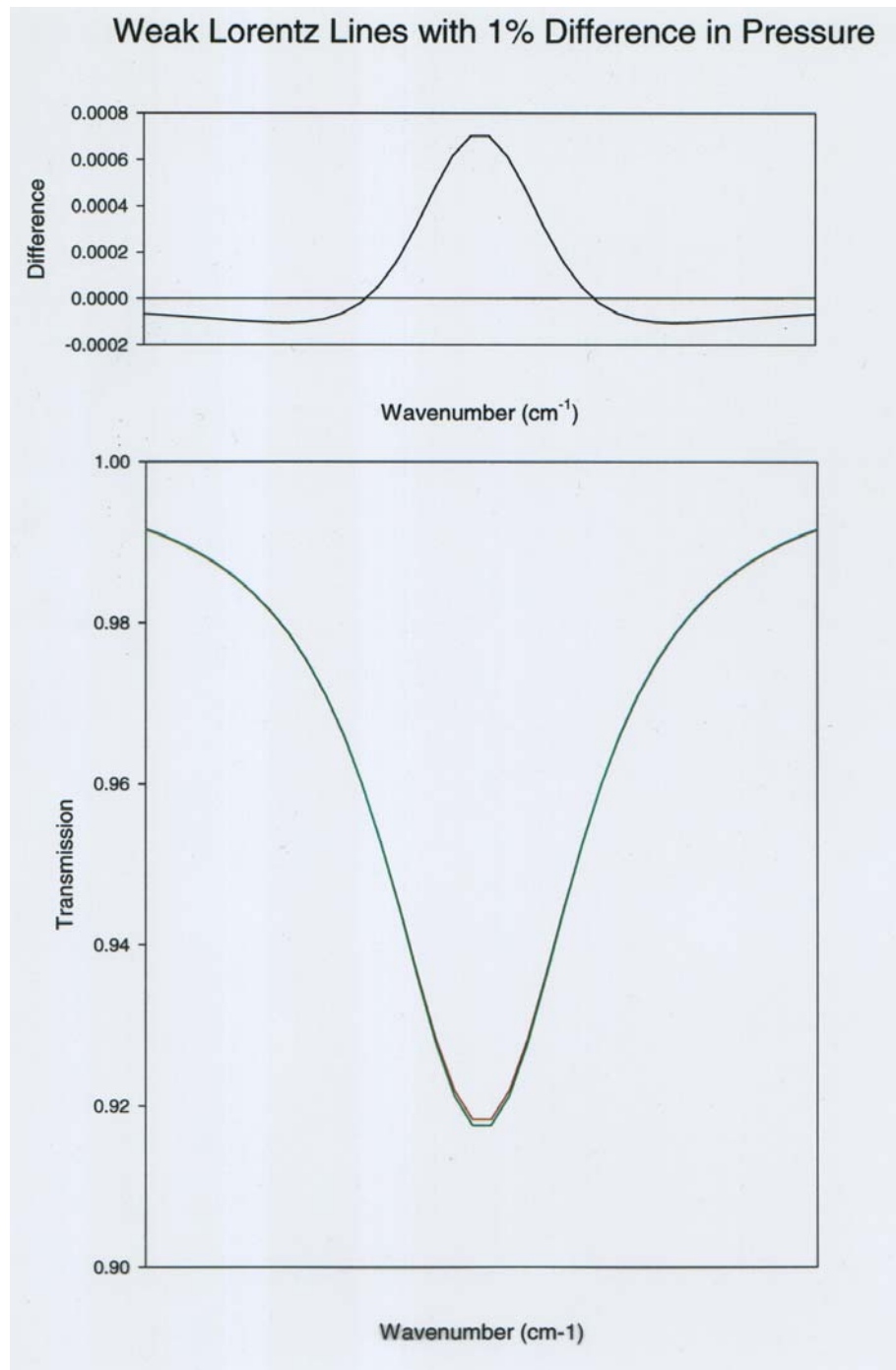


Figure 14

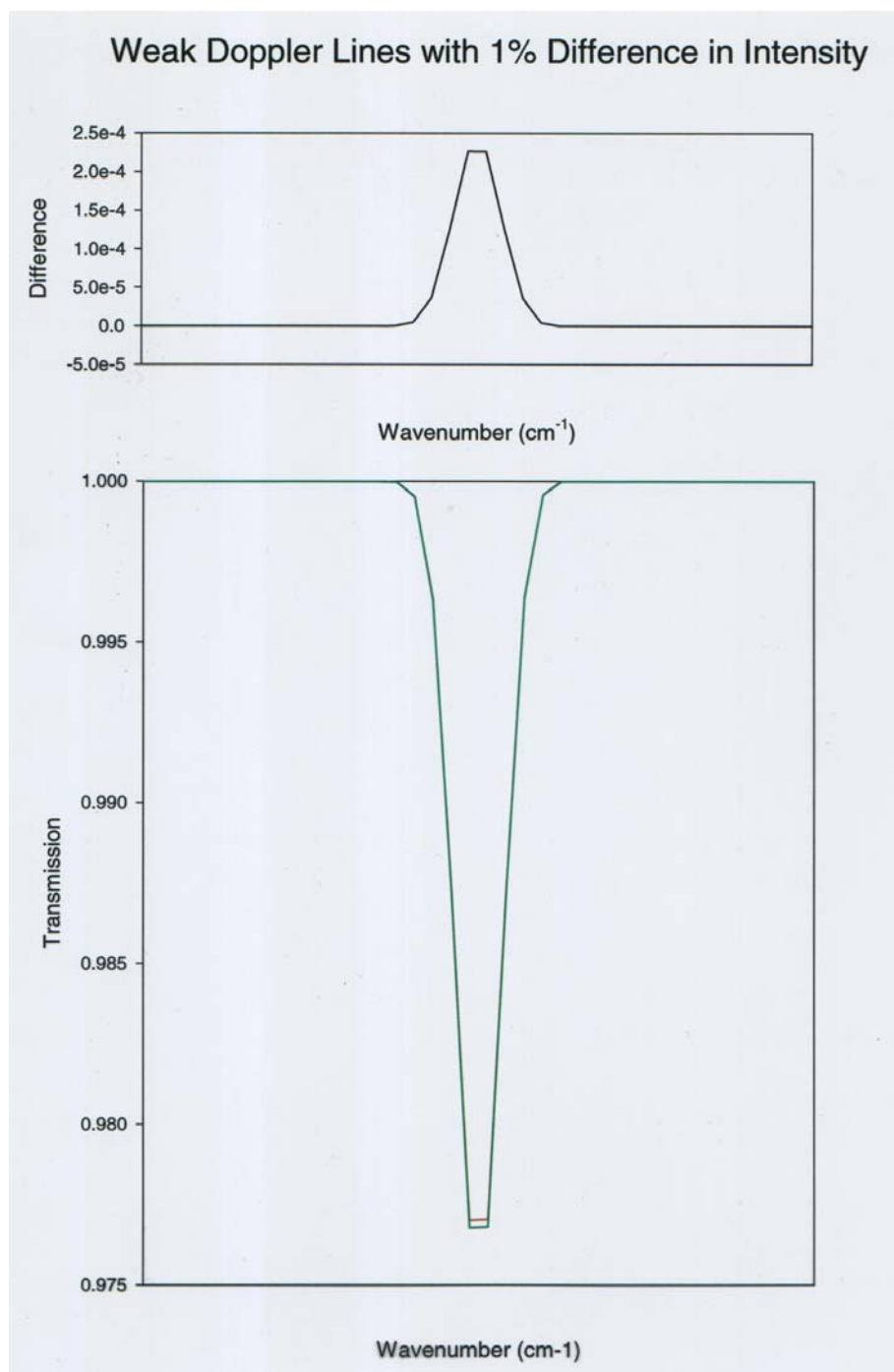


Figure 15

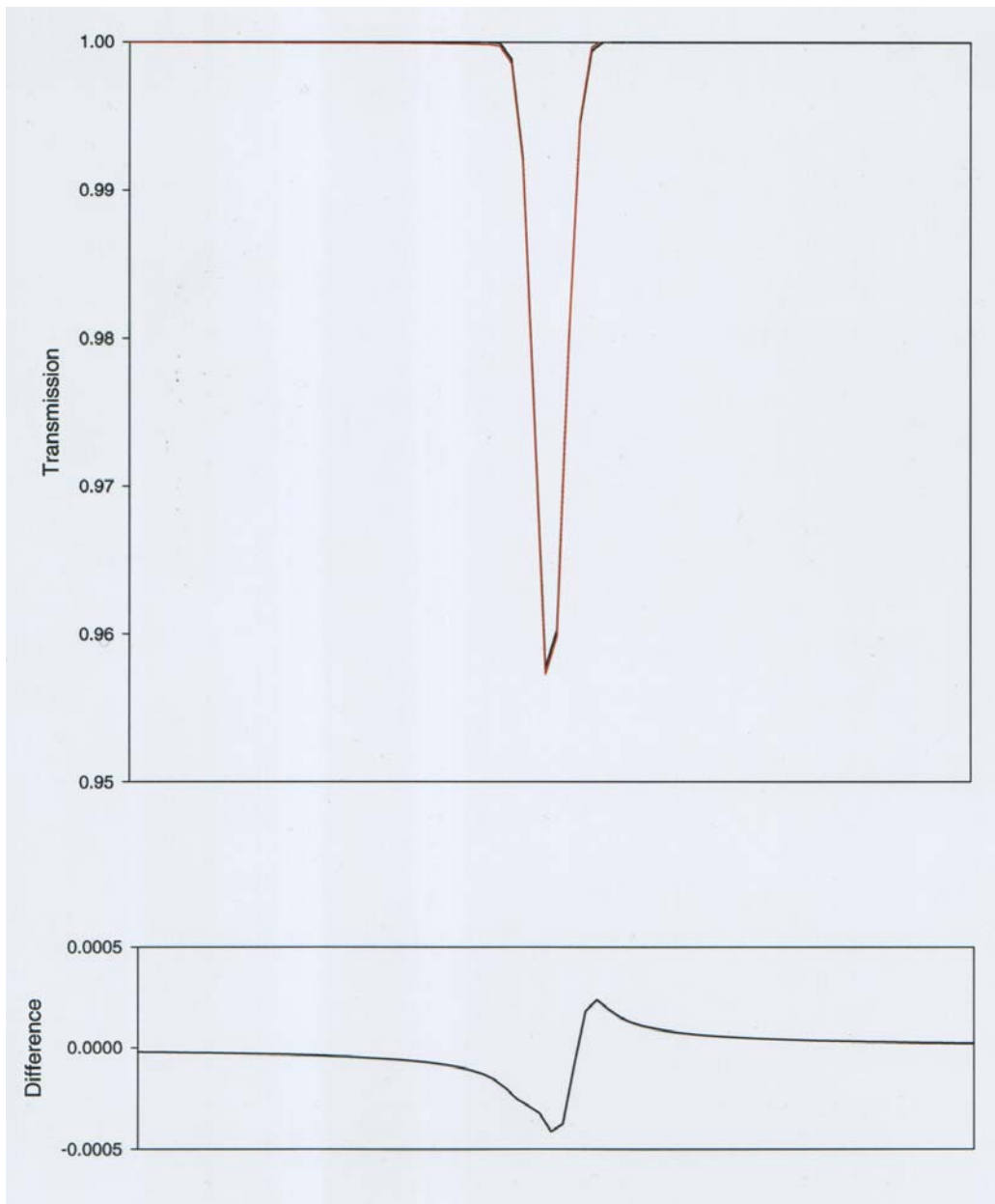


Figure 16

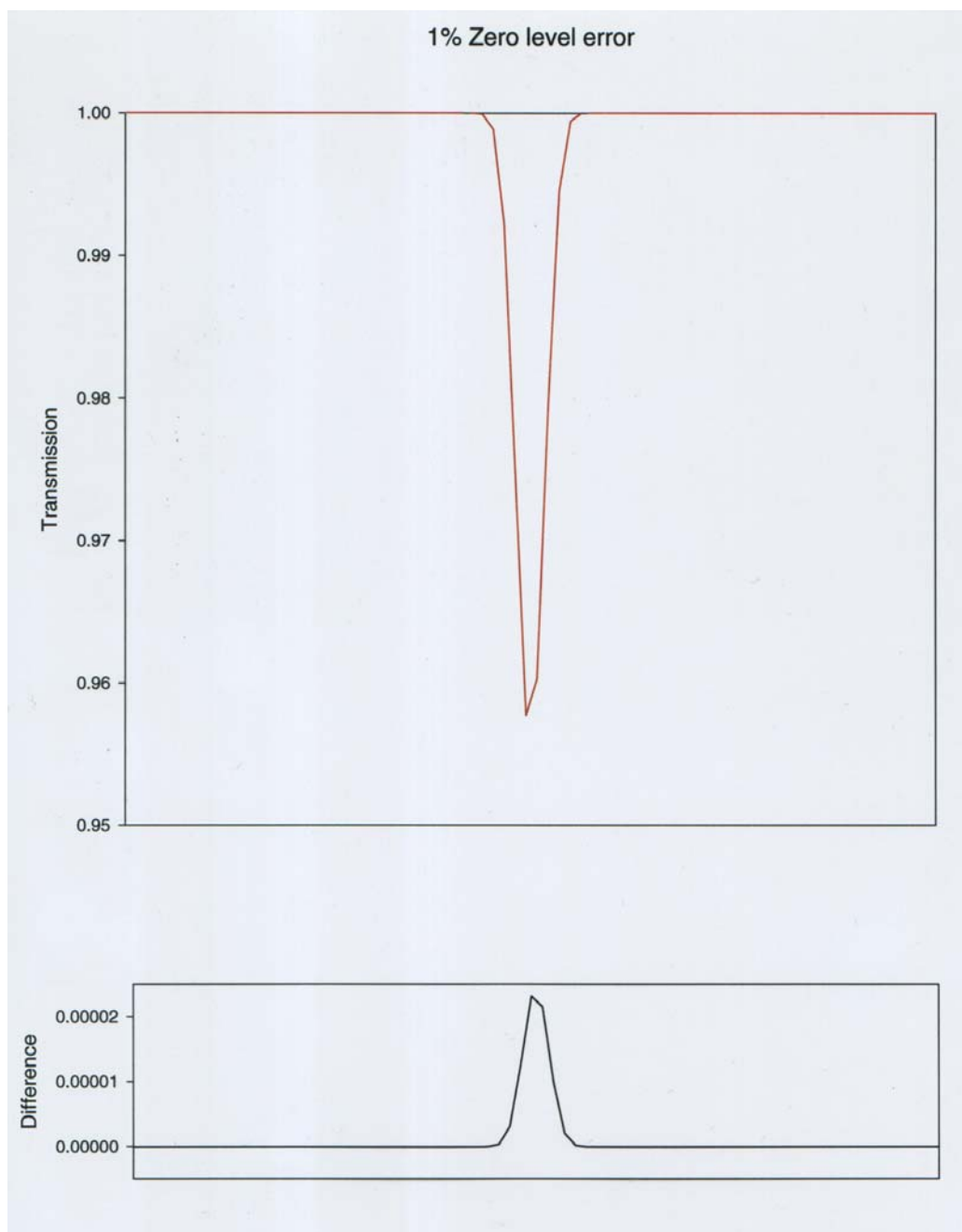


Figure 17

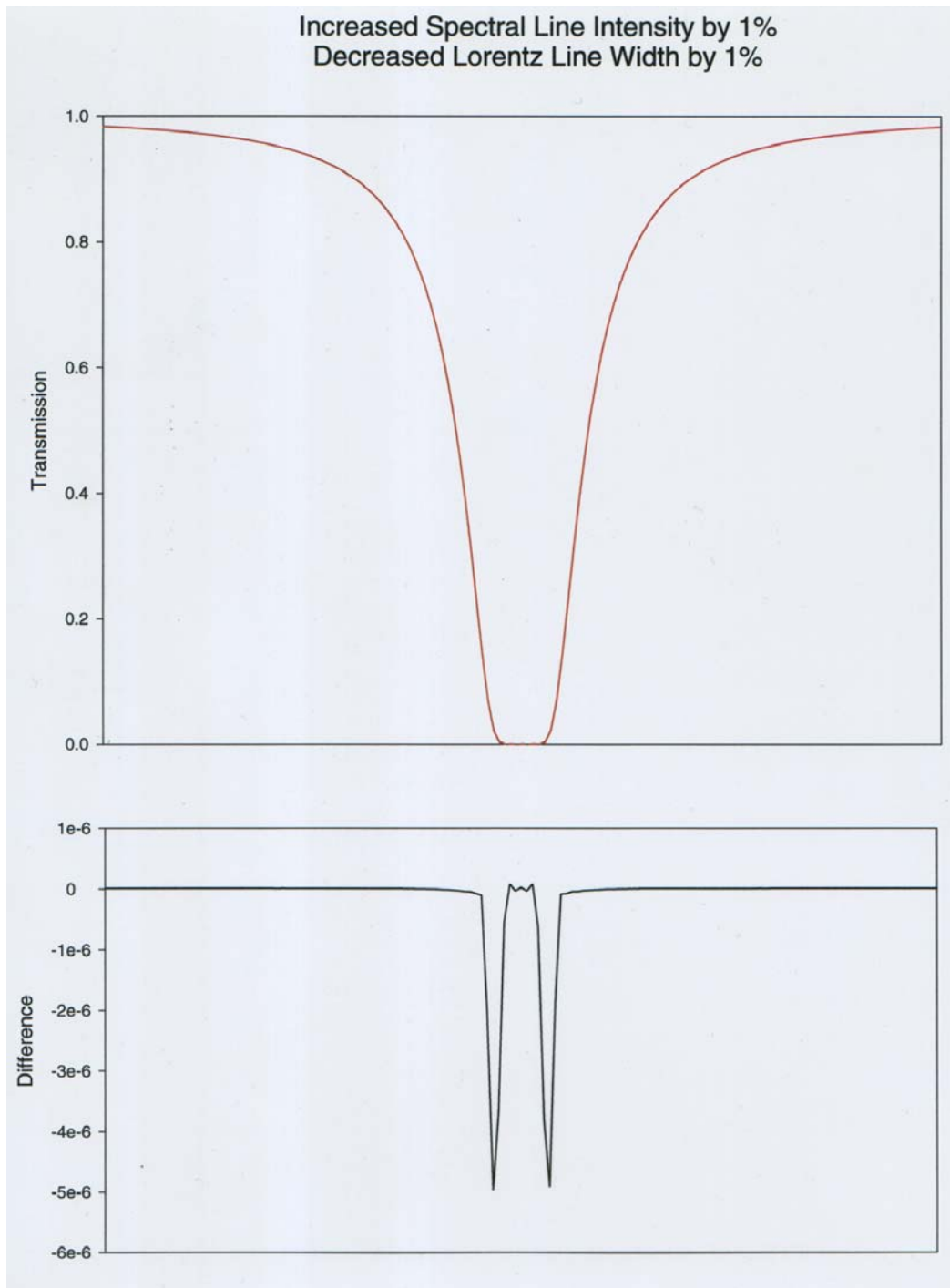


Figure 18

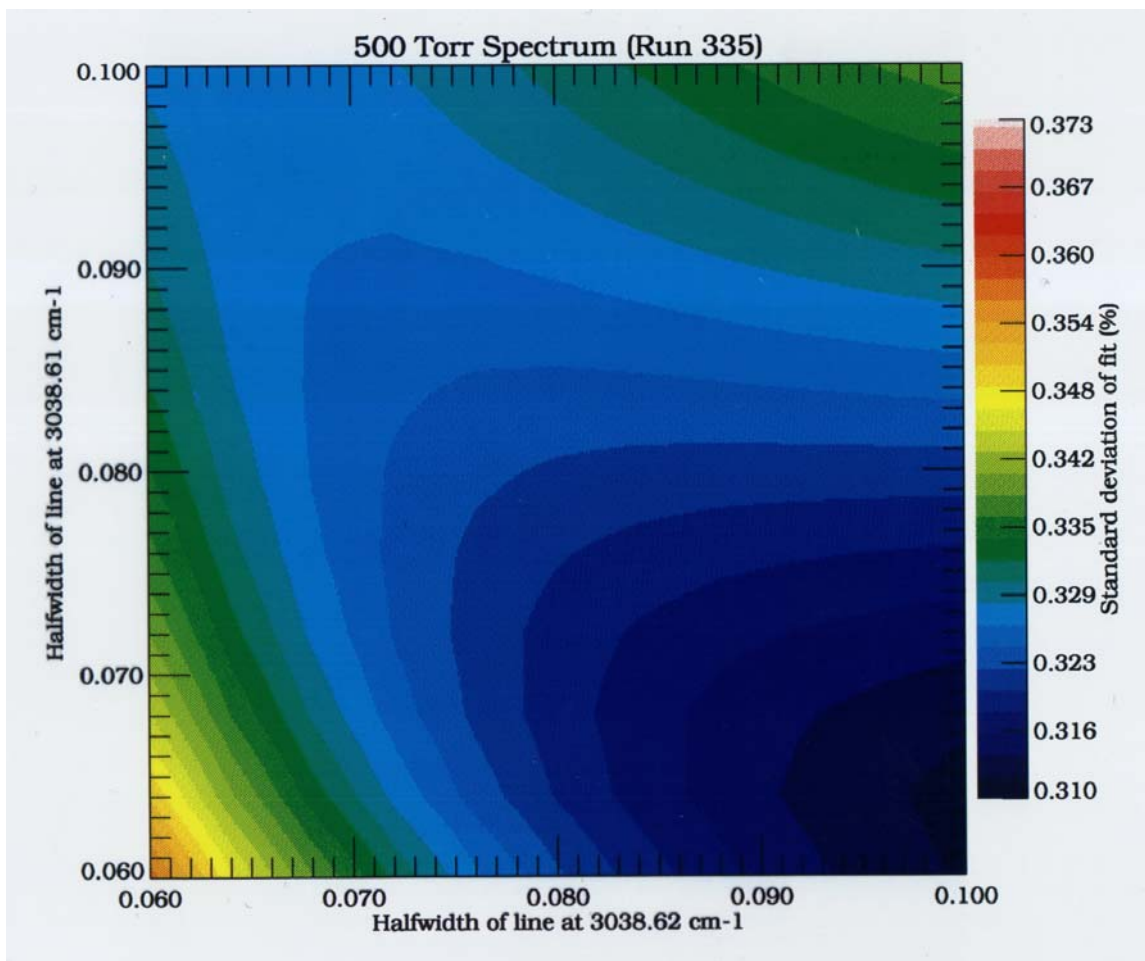


Figure 19

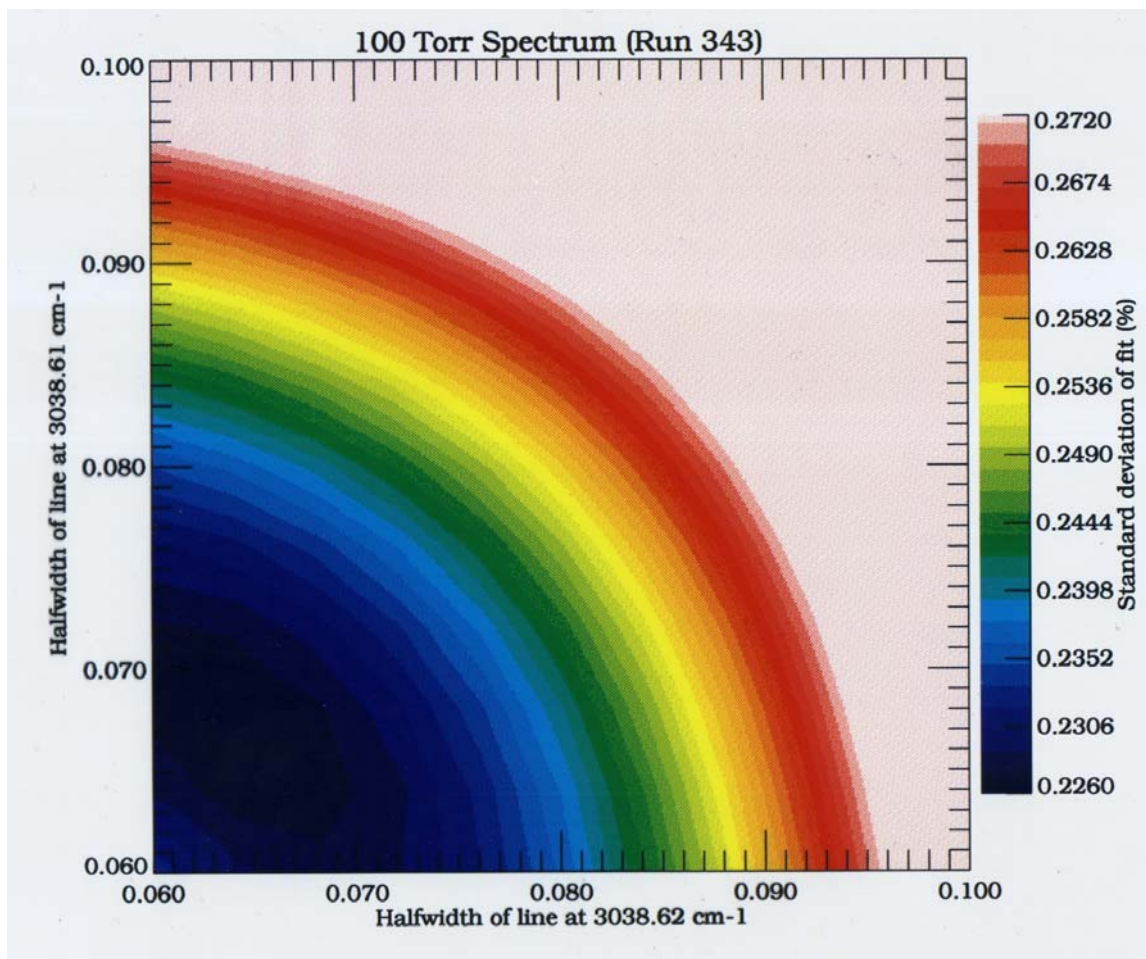


Figure 20

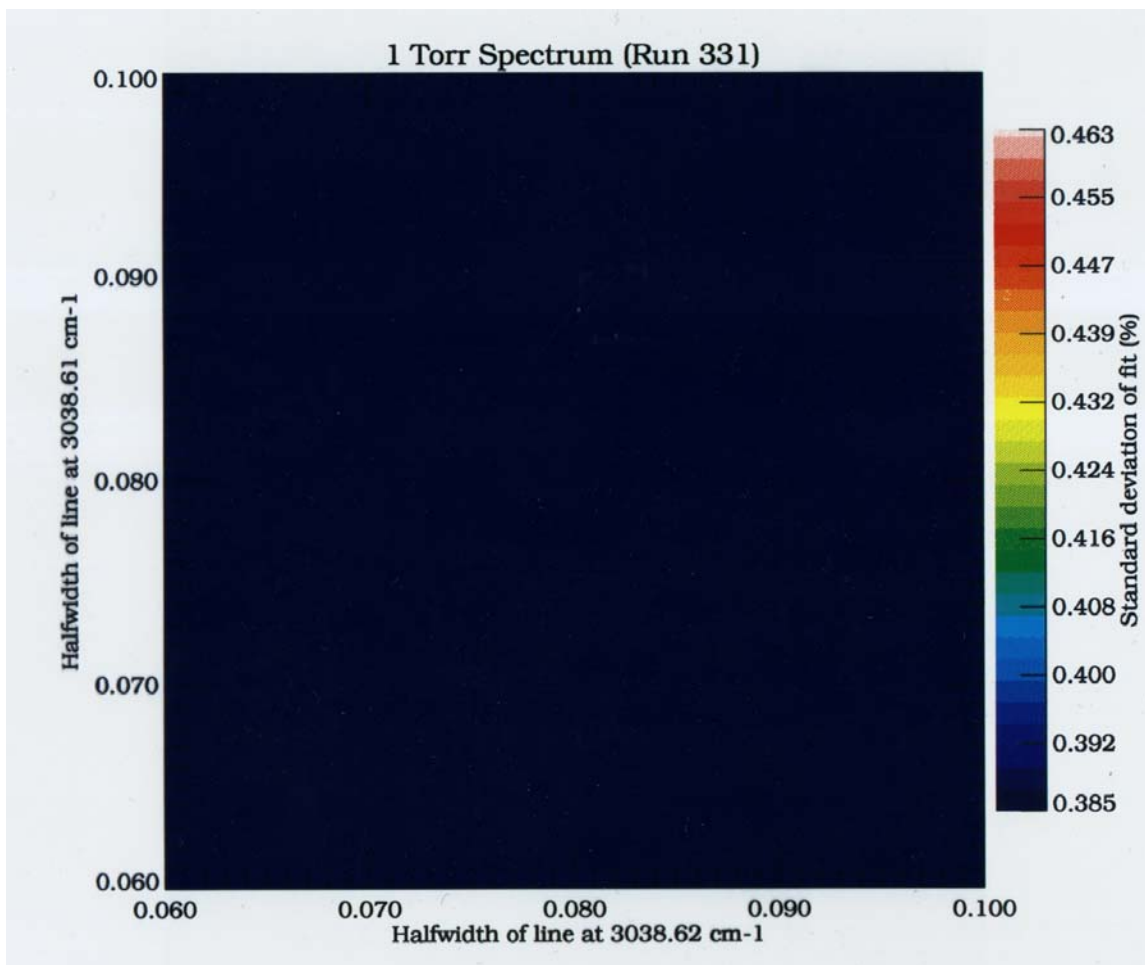


Figure 21



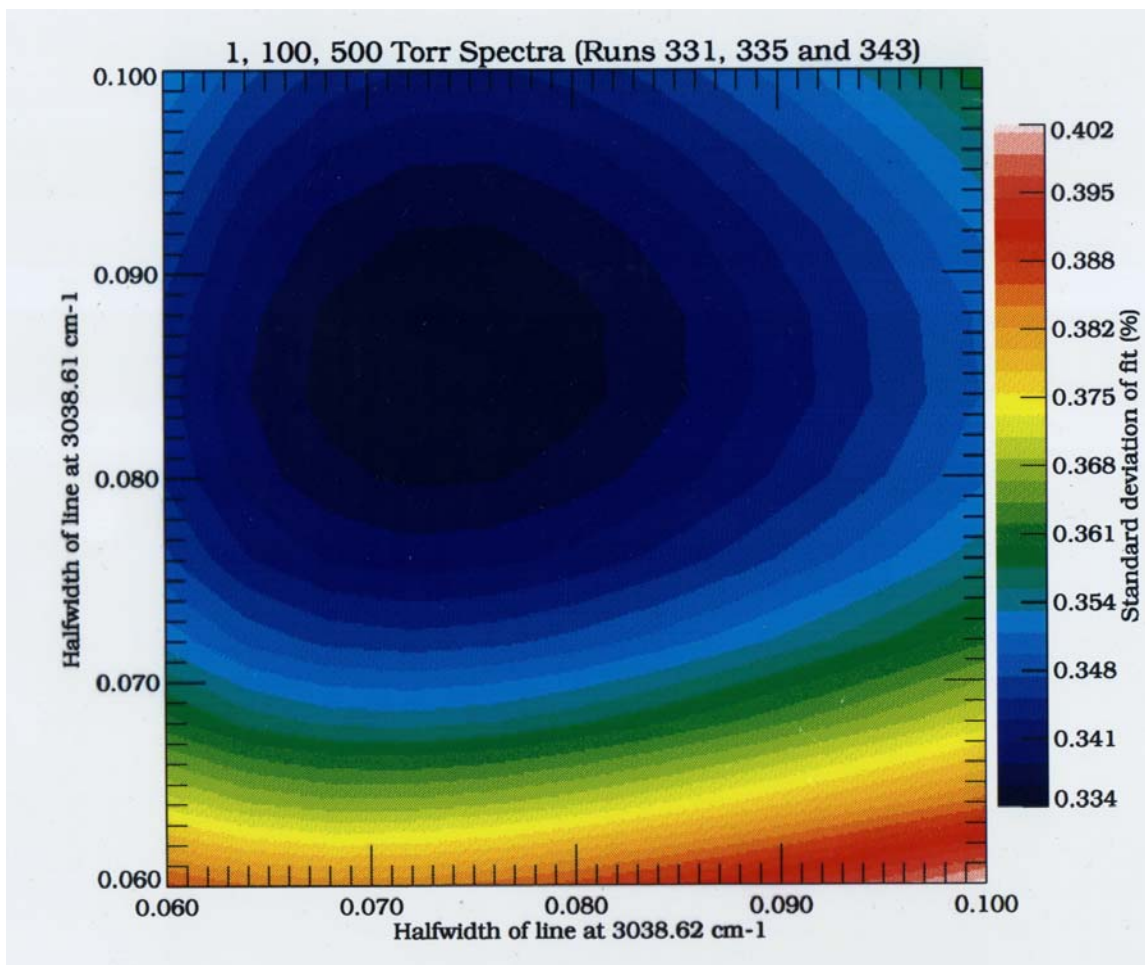


Figure 22

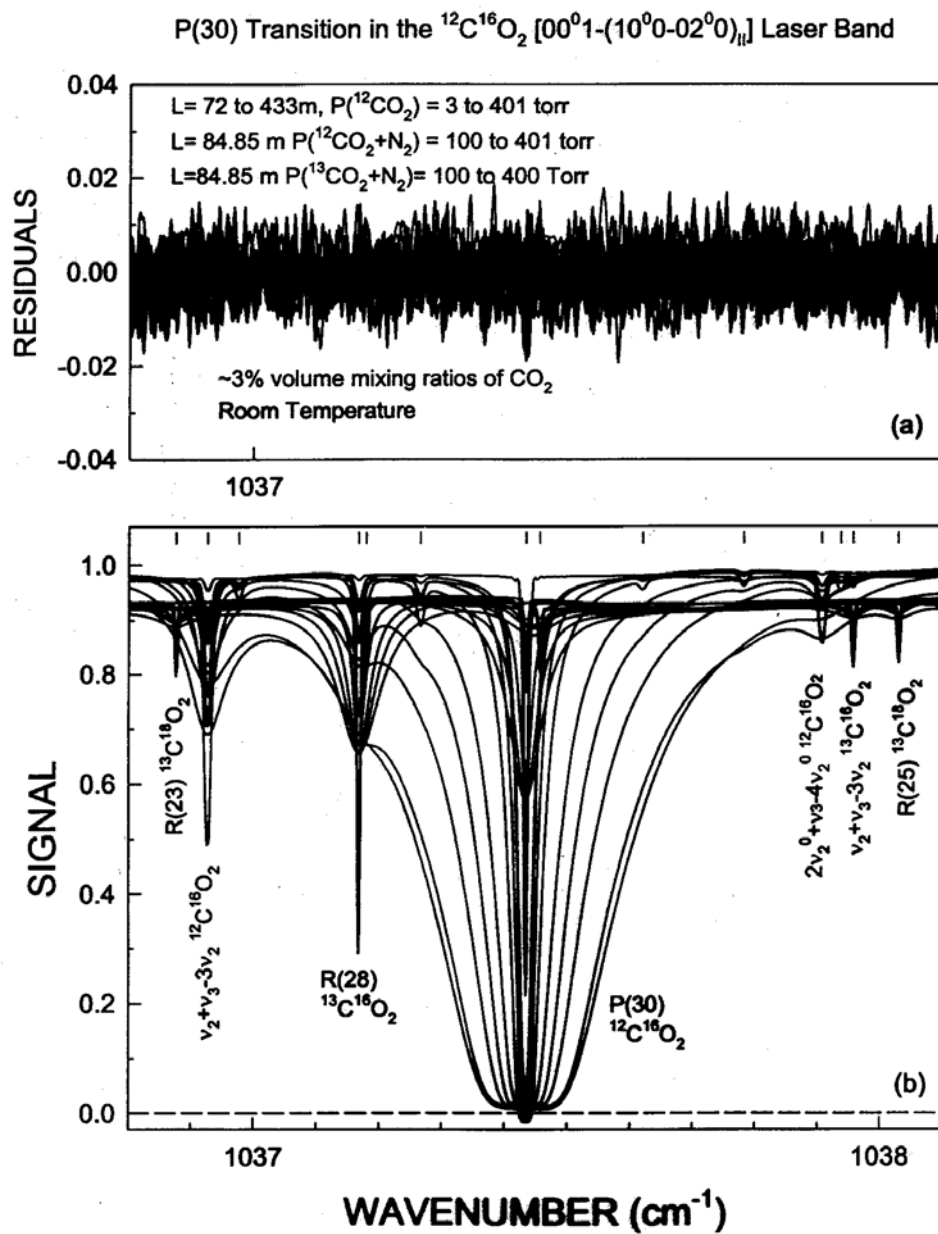


Figure 23

$^{13}\text{C}^{16}\text{O}_2$  and  $^{12}\text{C}^{16}\text{O}_2$  transitions near  $2275\text{cm}^{-1}$ .

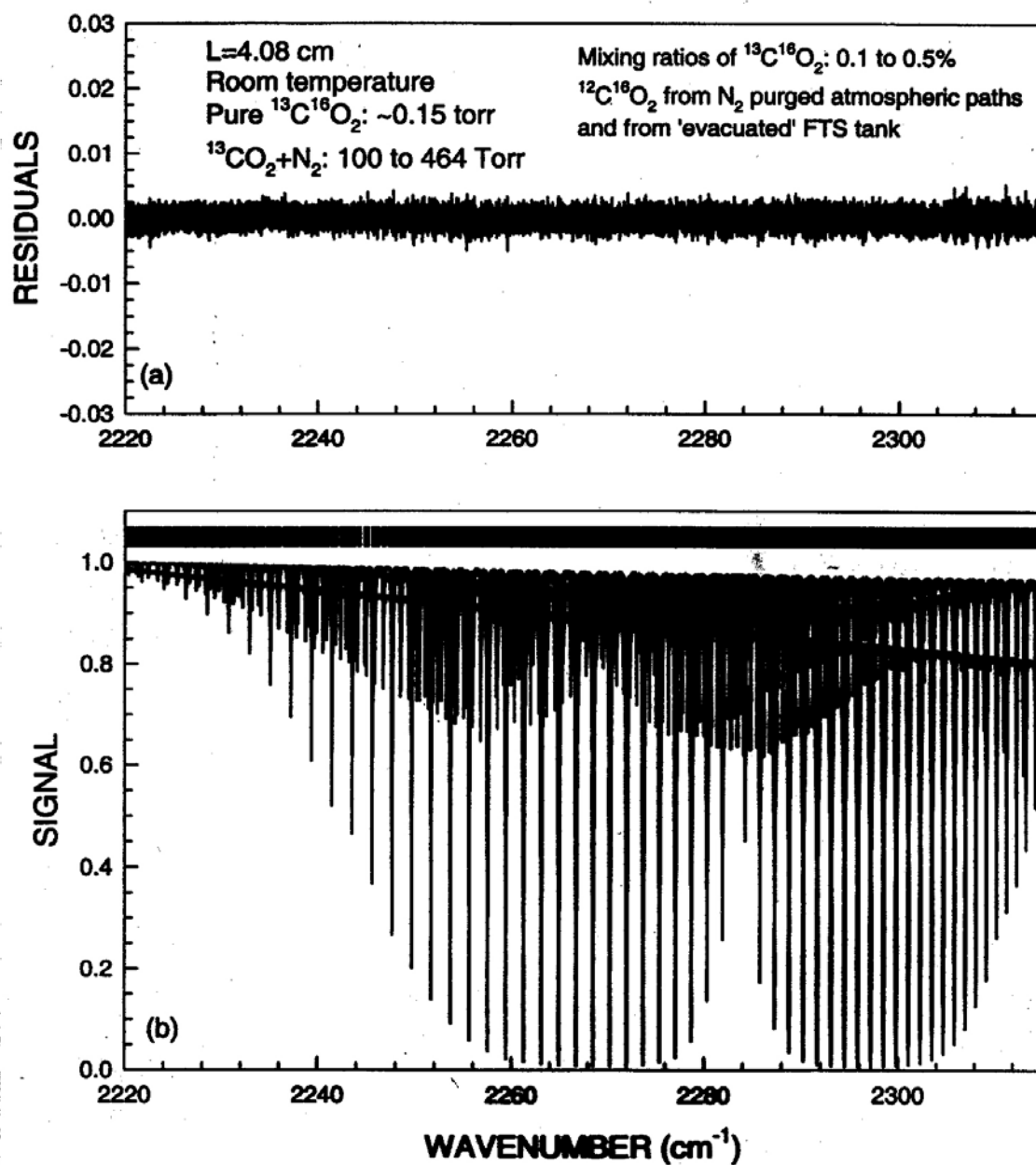


Figure 24

$\nu_3$  Bands of  $^{12}\text{C}^{16}\text{O}_2$  and  $^{13}\text{C}^{16}\text{O}_2$  near  $2350\text{ cm}^{-1}$

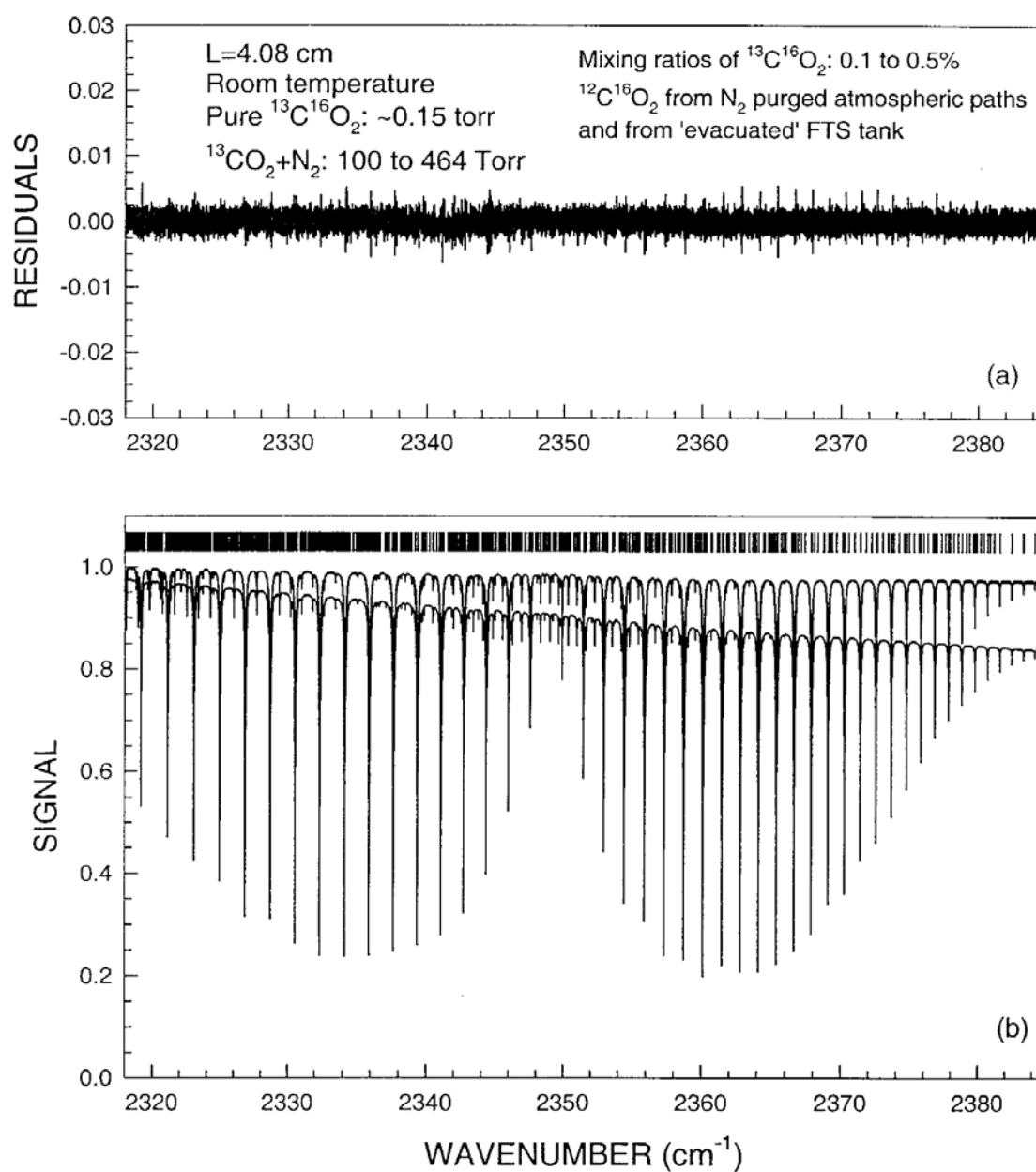


Figure 25

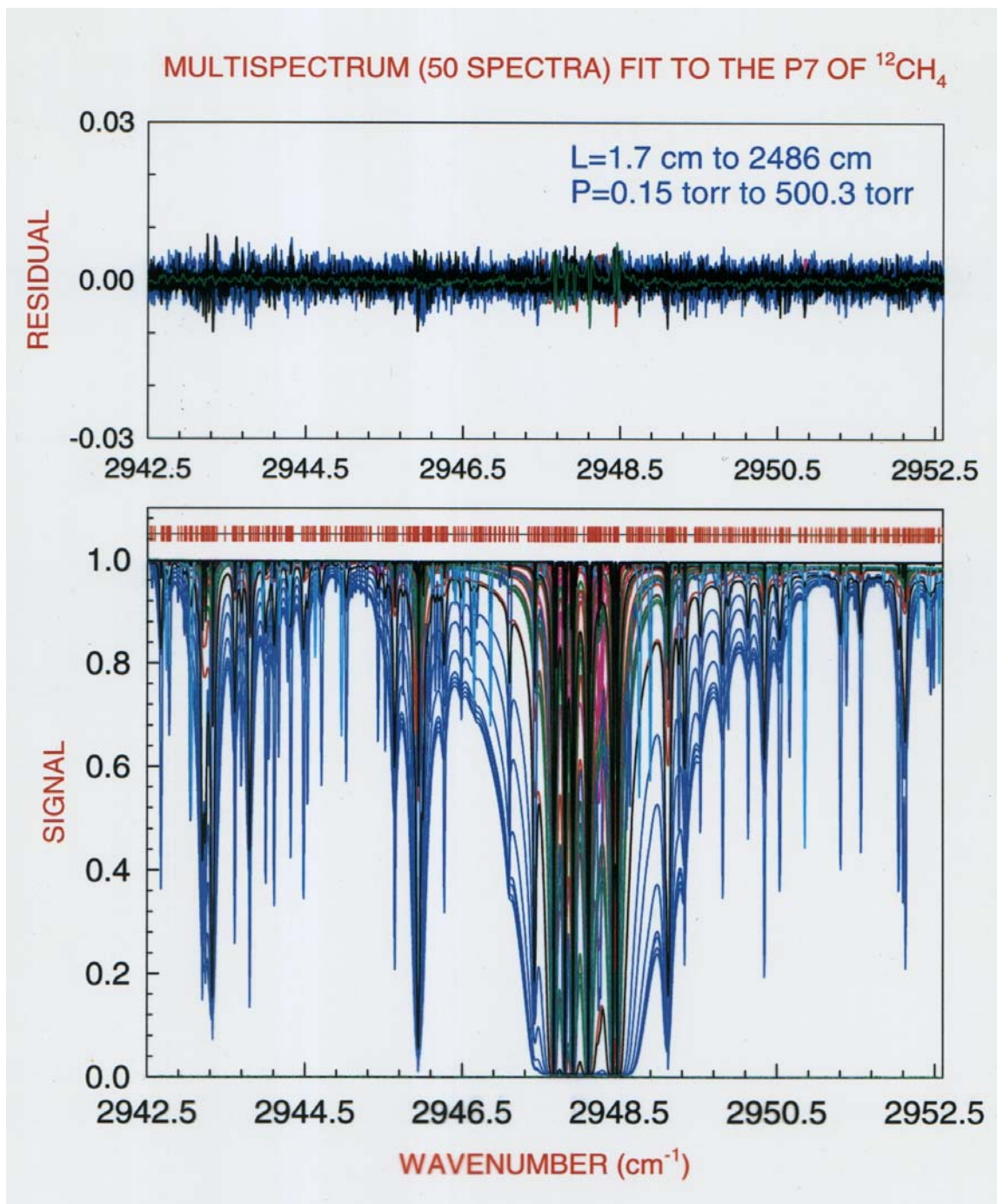


Figure 26

## **Methane Fit around the P7 Manifold of the $\nu_3$ Band**

**Spectral region fit:  $10.0\text{ cm}^{-1}$**

**Number of spectra: 50**

**Spectral resolution:  $0.0014$  to  $0.01\text{ cm}^{-1}$**

**Path lengths:  $1.7\text{ cm}$  to  $24\text{ m}$**

**Pressure:  $< 1\text{ Torr}$  to  $\sim 500\text{ Torr}$**

**Temperature:  $-60^\circ\text{ C}$  to  $+25^\circ\text{ C}$**

**Number of fitted points:  $\sim 100,000$**

**Number of spectral lines included: 825**

**Number of unconstrained parameters: 961**

**Computation time:**

**2 minutes 45 seconds per iteration**

**+ 1 minute**

Figure 27

## MULTISPECTRUM NONLINEAR LEAST-SQUARES FITTING TECHNIQUE

This is an extended version of the nonlinear least squares fitting technique developed for the simultaneous fitting of multiple spectra.

This technique for fitting simultaneously numerous high-resolution laboratory infrared absorption spectra recorded under various experimental conditions has been developed by D. Chris Benner of the College of William & Mary.

- 1) The smaller number of fitted parameters in this procedure as compared to fitting one spectrum at a time improves the determination of spectroscopic parameters.
- 2) A more reliable evaluation of the errors associated with the solution is possible.
- 3) Correlation among fitted parameters may preclude their determination from a single spectrum fit. If correlation differs from spectrum to spectrum, however, separation of these parameters is often possible when including the spectra in one solution.
- 4) Over fitting is also avoided when combining spectra with sufficiently different experimental conditions.

Figure 28



## Laboratory Uncertainties

1. Pressure Gauge
2. Converging beam
3. Etaloning
4. Calibration of Frequency Scale
5. Isotopomer mixing ratios
6. Quality of mixing of gases
7. Outgassing (especially water)
8. Temperature and temperature uniformity

Figure 29